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EDITORIAL

Corrosion

CORROSION is a very important branch of chemistry and it is responsible for a voluminous literature. We need not be surprised at this: ›ur surprise is that there is not a far greater literature, ›r corrosion really denotes the chemical changes of ›etallic substances brought about by their exposure › gases, liquids, and solids, sometimes to only one ›f these three, sometimes to two, sometimes to all, ›nder different conditions of temperature and of ›very other circumstance. Hence corrosion is nearly ›o-extensive with the chemistry of the metals and *heir alloys, though in practice we mean by corrosion* ›he chemistry of iron and ferrous alloys, copper and its ›lloys, nickel and its alloys, aluminium and its alloys, ›ad and its alloys, zinc and its alloys, and so on. Even ›ith this restriction the subject is a considerable one ›nd it remains considerable if it is further limited to the ›hemical changes made in these substances by the air ›nd the various gases that mankind pours into the air, ›y water and the aqueous solutions that are of common ›ccurrence, and by such solids as the earth in which ›etallic rods and pipes are laid. No general statements ›bout corrosion, its nature, causes, and prevention, ›ill be of much assistance to us and the many attempts ›hat have been made to discover the main principles ›f corrosion are about as valuable as the attempts to *›scover the main principles that guide mankind* ›wards progress and civilization, assuming that these ›ates exist. Dr. Bengough in his careful and long ›ubilee Memorial lecture, of which we publish the ›rst portion this week, calls attention to six factors ›lating to the metallic substance itself, which influence ›s rate of corrosion by a salt solution, and eight other ›ctors which belong to the environment and also ›fluence the rate of corrosion. Workers on corrosion ›ave for a long period studied special features and ›ecial circumstances and have collected data of much ›lue *and interest*. Our knowledge of corrosion has ›een greatly increased by such work and yet, it seems › us, that Dr. Bengough has taken a more logical view ›f the problems than any other worker in this field ›nd has done more than any one else to indicate the ›traordinary degree of complexity of corrosion and ›e necessity for a separate study of each of the fourteen ›ctors that he has enumerated. The problems are ›metimes rather perplexing; one piece of cast iron ›ill be hardly touched by sulphuric acid of a certain ›rength, while another piece of apparently similar cast iron will be rapidly eaten away. Dr. Bengough tells us that the sea-water at Auckland is very different from the sea-water at Halifax; chemically we suppose the composition of the two solutions may be practically identical so far as analysis is concerned but the other factors may differ enormously. We have read many papers on corrosion, without professing to have studied the topic with any great attention; while many papers have *contained matter of great importance and interest* we do not recollect any paper that has handled the topic so logically and lucidly as Dr. Bengough has done. We think that it is a milestone, or indeed a landmark, *in the literature of the subject that will be welcomed* by those who have studied corrosion carefully for many years and will be a guide and an inspiration to those who will henceforth make excursions into this excellent field of research.

A New Lead Alloy

We publish this week an interesting paper by Messrs. W. Singleton and Brinley Jones on a new alloy of lead containing about 0·06% of tellurium. It appears to have two remarkable properties; it is much less liable to corrosion and it has greater toughness and tensile strength than the ordinary familiar soft lead. We gather that if it is hammered or squeezed or rolled when cold its tensile strength increases, a property of some importance in connexion with water pipes that are exposed to the liability of freezing. The pressure caused by the formation of a cylinder of ice within the pipe makes the pipe more resistant to such pressure than it was: the explanation is not quite similar to the effort of the foot to protect itself from an undue pressure by the boot; this pressure tends to harden the skin of the foot and produce a corn. The pressure on the tellurium-lead pipe toughens it without hardening it and the pipe can stand many more freezings than an ordinary lead pipe before it is compelled to burst. Chemists are aware that selenium compounds have been found to have a great influence to protect magnesium from corrosion and it is interesting to know that so similar an element as tellurium reduces the corrosion of lead to about one-seventh of what it is in the case of pure lead. We gather from the paper that the beneficial effects of tellurium are pronounced with the small percentage that we have mentioned but there is no indication that a higher percentage of tellurium confers any higher measure of benefit.

Anthocyanins

The books and catalogues which guide our choice of plants, whether for the herbaceous border or the rockery, have in the past been content to indicate the colour of the flower, and perhaps the height of the plant. Thanks to the efforts of the Oxford family Robinson, who like their legendary prototypes continue to make full use of every opportunity, it will soon be possible to indicate also the name of the anthocyan which produces the colour, so that the entries in the future will read something like this: *Aubretia deltoides*, "Fire King," reddish-violet flowers, contain a 3:5 dimonoside of cyanidin, or *Colchicum autumnale*, the pale mauve flowers are malvidin-3-bioside. The achievement is an amazing one, and it is worth while trying hard to understand it: this should be obligatory for every gardener who has any knowledge of chemistry. The anthocyanins of many hundreds of plants have now been identified by the Robinsons, and it is possible to give a general idea of their differences. It will be remembered that the anthocyanidin complex consists of two rings, each containing six carbon atoms joined to a ring containing 5 carbons and oxygen; the complex contains 15 carbons in all. There are only three types of anthocyanidin, depending on whether one of the C_6 rings contains one, two, or three hydroxyls. There is also a hydroxyl at position 3 in the ring containing oxygen, and one or sometimes two hydroxyls at positions 5 and 7 in the other C_6 ring. Of these positions 3 and 5 are the interesting ones, and it is obvious that a substituting group will have different properties, according to which position it enters. The anthocyanins as they occur in the flowers are all glycosides; often one molecule of glucose is attached, always at 3. When two molecules of glucose are involved, they may be linked as a bioside and again attached at 3 or 5, or two units of the sugar may be separately attached, one at each position. The difference is simple enough, but as a result of it nature has five modifications of the same anthocyanidin complex to use in different plants and can have as many more by varying the sugar, *i.e.*, by substituting rhamnose for glucose. Thus, taking for example cyanidin as the anthocyanidin, it has been identified as 3-pentoseglycoside in deep crimson flowers of *Dianthus*, as 3:5-dimonoside in a magenta-shaded dianthus, as 3-bioside in the rose-red *Dieletyra*, as 3-glucoside in the heath. The other type of variation, that is to say in the aglucone instead of the sugar, is exemplified by the nasturtium, one form of which has been found to contain derivatives of pelargonidin in the flower petals, of cyanidin in the calix, and of delphinidin in the leaves. The experimental technique of purifying and identifying these anthocyanins, in part based on their distribution to amylalcohol, is not a complicated one, and it is applicable to small quantities. None the less, the skill displayed in the identification of these colours compels our admiration, whilst our faculty to wonder is overwhelmed in contemplating the simplicity with which nature rings all her infinite variety of changes in the colouring of the flowers. Though the story may appear complex enough in the few words which are all we can devote to it here, it will prove far less so with the formulæ before one, and there can be few chemists with knowledge of organic chemistry who will not feel proud that it has been possible to unravel this secret of the flowers. When the day comes to put a synthetic carnation in our buttonhole, it will be tinted with the genuine cyanidin glycoside made in the laboratory.

Applied Chemistry Reports

The seventeenth volume of the Annual Reports on the progress of applied chemistry has just appeared. To publish so useful a book, of more than 700 pages, containing an epitome of the developments of twenty-six divisions of applied chemistry throughout the year 1932, and to publish this within seven weeks of the close of the year, is an achievement that is very creditable to all those who are in any way responsible for its production. We think that several of the chapters are a little less condensed and therefore rather more readable than they used to be two or three years ago. This seems to us to be a great improvement for we know of no other volume that covers this ground at all adequately and it is used not only by the experts who wish to see the progress in their own branch of the science but also by the experts who wish to see the progress in the other branches of the science. The chapters have been prepared by recognized authorities on the particular subject; in many of the chapters changes have been made from those who prepared the corresponding chapters a few years ago. During the last year or so there have been changes in the world of terrible significance; who would have believed a Cassandra who a year ago predicted the present conditions in the United States, in Germany, in Manchuria, and in many other countries? Whether such great changes are fortunate or otherwise it is not for us to say here. They are very disturbing to us who live in this country and dislike the changes partly because we do not really understand them. On the other hand they are much less disturbing, so it seems, to those who live in those countries, who see from day to day the changes coming about and who are obliged to adapt themselves to them and do adapt themselves to them speedily and philosophically. However such events may be regarded it is pleasant and refreshing to read of the steady and orderly progress of science the workers in which pursue their study with the abstraction that history credits to Archimedes. We read in these reports of the increased use of Diesel engines and the growth of the cellulose and textile industries in Russia and Japan, of the creaseless cellulose fabrics of the Tootal Broadhurst Lee Co., of the new £3,000,000 plant for basic Bessemer steel in this country and the spun cast-iron pipes made by the Staveley Coal Iron Company. There is a very valuable account of progress in the corrosion of non-ferrous metals, a topic of interest and importance and some useful information on synthetic rubber. There is a convenient account of the modern work on vitamins and the bile acids and indeed these Reports do cover a very wide range. Students of all ages should certainly refer to these books, should buy them and treat them as the most up-to-date text-books available.

CORROSION OF METALS IN SALT SOLUTIONS AND SEAWATER

JUBILEE MEMORIAL LECTURE, 1932–1933

By Dr. G. D. BENGOUGH

I am fully conscious that I am standing to-night in the place of very eminent predecessors who have already given Jubilee *Memorial Lectures*. Since I cannot hope to emulate them in quality, I shall do so in quantity, and this lecture is timed to last four hours. I beg that you will not be unduly alarmed for you will all be able, without discourtesy, to retire to bed at your normal time, since only the first quarter will be given to-night, under the subtitle "The Measurement of Corrosion." The second part will be inflicted on the Glasgow and Edinburgh Sections on November 25, and the third, subtitled "The Distribution of Corrosion," on the Manchester and Liverpool Sections on December 2. The last part, unless I am previously warned off the course, will be given at Newcastle on January 13. The whole set will present a picture of the mechanism of corrosion in the particular conditions studied, and will include a description of the experimental methods used to build it up.

Broadly, the methods of measuring corrosion may be grouped in three classes:

(1) Tests under actual working conditions; *Industrial tests.*

(2). Tests in conditions believed to be similar to but not actually industrial conditions; *Field tests.*

(3). *Laboratory tests.*

Many people snort contemptuously when they hear mention of laboratory tests; and, obviously, industrial tests are the ultimate standard of reference for all corrosion work; but these tests must be undertaken with caution because of the time, expense, and possible danger that may result from metal failure. They should therefore be approached gradually through a preliminary series of field and laboratory tests.

Field tests should be designed to give as close an approximation to severe working conditions as possible; here lies the great difficulty. Their special value is that the failure of any material may be neither so expensive nor so dangerous as in an industrial test. Some of the problems involved in field tests may be illustrated by the work of Dr. Newton Friend (part of it done in conjunction with the Institution of Civil Engineers) on "*The Deterioration of Structures in Seawater.*" The procedure was to expose weighed bars to seawater, either immersed continuously or between high and low water marks, for periods of several years. Bars were removed at intervals, scraped free from marine growth and corrosion products, wire brushed, weighed, and the depths of any pits measured; some tensile tests were included. Experiments were made in different parts of the world, Halifax, Auckland, Colombo, Plymouth, Southampton Docks, and Weston-super-Mare.

It is impossible to deal with the whole research, but reviewing some of his results after five years' exposure Dr. Friend stated that "the half-tide and immersed bars at Auckland were less seriously attacked by localized corrosion than those at Halifax." "Steel B which has a high sulphur content has not proved so seriously inferior at Auckland as it has at Halifax." "At Auckland the high-nickel steel specimen lost least in weight of all the metals . . . ; but at Halifax the cast irons proved slightly superior to the high-chromium and nickel steels." The conclusions seem to be that the Auckland conditions were rather less severe, but that the various materials could not be arranged in the like order of merit at the two ports. A similar result to the latter has been reached by a Committee of the American Society for Testing Materials by experiments on several varieties of steel in New York Harbour and Key West, Florida.

Table I shows results of two field tests by Friend in this country. It will be noticed that at Weston aluminium lost little weight, while steel, wrought iron, copper,

TABLE I (based on Friend's results)

Losses of Weights, g.

	I Weston-s.-Mare 4-year test		II Southampton Dock 3-year test	
		Deepest pit, mm.		Deepest pit, mm.
Mild steel ...	173	0·95	51	Uniform attack
Wrought iron	137	1·00	41	
Aluminium . .	47	5·81	0·15	Negligible
Lead (soft) ...	29	—	5	—
„ (antimonial) ...	22	—	4	—
Copper ...	128	Uniform attack	3·5	Uniform attack
„ (arsenical) ...	120		3·7	
Zinc ...	133	0·89	14·3	1·3; 1·35
	No visible adherent faunæ or weed		Covered with mud and faunæ	
	Rapid current and possible scouring		Slowly moving water	

and zinc lost much more, and the last three about the same weight; at Southampton aluminium was almost unattacked, copper was highly resistant, with zinc and iron well behind. As regards pitting, aluminium at Weston was far the worst, followed by zinc and iron; the other metals showed practically no pitting.

Fig. 1 shows the appearance of lead and nickel-steel bars from Southampton; the lead is coated with shells, and oil from ships had helped mud to stick to the metal in the slowly-moving waters of the dock. Shell-fish adhered to all the bars except copper, and, when dead, they seemed to localize corrosion on alloy steels, nickel, and nickel-alloys.

It is clear that the results of such tests are very difficult to interpret. We cannot assume that the losses of weight and depth of pitting were in linear relation to time, but we should like to predict from them both the rates of general corrosion and of pitting in structures placed in similar conditions. But what are similar conditions? We do not really know the factor which controlled either the general corrosion rate, as indicated by loss of weight, or the localized rate of pitting. Did the reactivity of the metals decide these? Was pitting due to some local factor in the metals themselves, or in the conditions? Or was the rate of oxygen supply the controlling factor, and, if so, was this determined mainly by the scouring action at Weston and mud at Southampton?

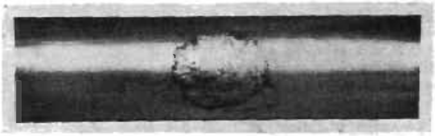
A detailed examination of the data based on knowledge otherwise acquired suggests that this last may

be broadly true, but that there were interfering factors, and individual metals were affected to different extents. Attempts to interpret the results in the ill-defined conditions of such tests can be little more than guesses unless we already have a comprehensive knowledge of the factors which control corrosion rates, obtained from experiments conducted in strictly defined conditions.

Here lies the justification of laboratory tests, for in these we can ascertain the factors which actually control corrosion rates. In the past, laboratory tests have often been used merely for the purpose of ascertaining how much metal will corrode in an arbitrarily fixed time, a result of limited value since corrosion-time curves have not been obtained. Further limitations are that the conditions in most laboratory tests have neither been similar to those in practice, nor strictly defined, nor comparable with those of other authors, nor have separate hydrogen determinations been made. If, however, experiments be arranged in such a way that we can get corrosion-time curves and also ascertain *the factor that controls the corrosion rate*, then we have a result of much greater significance, for we can make strict comparisons and may eventually be able to adjust the value of the controlling factor and correlate it with any industrial conditions which can be broadly specified. For such work, accurate methods of measuring corrosion are essential.

The idea is present in the minds of many chemists that corrosion is affected by so many erratic factors (such as metallic heterogeneity, the formation of boundary films, concentration changes and convection currents) that it is essentially unreproducible and therefore unsuitable for quantitative study. The methods of many corrosion workers have rather encouraged this idea. Figures for reproducibility have rarely been given, but occasional admissions have been made that differences between duplicates may reach 50% or more; discussions have revealed the non-comparability of different authors' results, and sometimes of a single author's results given in different tables of the same paper.

This lack of reproducibility and comparability arises largely from absence of control of experimental conditions. The usual fluctuations of atmospheric temperature, for instance, are often permitted, and sometimes defended, on the ground that since they occur in industrial conditions they should also be allowed in the laboratory study of corrosion; but, since the effect of temperature fluctuations on corrosion rates is one of the things we want to know, we must first make experiments in their absence, and then when they are present in controlled amounts—a procedure attempted on[ly] recently and in one laboratory, so far as I know.



Nickel-chromium steel bar

[By courtesy of the Institute of Metals

FIG. 1

Lead bar covered with mud and shells

The main objects of the first part of this lecture ar[e] in fact, to assert the necessity of long-continued corrosio[n-] time curves of known reproducibility, and special[ly] studied for the elucidation of controlling factors; [to] suggest methods of making and reporting corrosi[on] measurements; to indicate some of the results alrea[dy] reached, and future possibilities for both normal a[nd] rationally accelerated tests. I shall deal only wi[th] corrosion in apparently stagnant salt solutions, partic[u]larly chlorides and seawater.

If you ask for a definition of the term stagnant, [I] shall adopt the arbitrary one, that *a stagnant soluti[on]* is one in which any movement that takes place is [by] diffusion only.

The more important study of obviously moving wat[er] can probably best be attempted rationally when f[ull] *information* is available about the quantitative eff[ect] of numerous factors in apparently stagnant conditio[ns]

since gross movement may change several factors simultaneously but to different extents, *e.g.*, the rate of supply of oxygen and the distribution and nature of corrosion products. A preliminary sorting out can be done more easily and accurately in apparently stagnant conditions.

The complicated nature of the problem may be illustrated by a list of the factors which have been stated by competent authors to influence the corrosion process (Table II). They are grouped in two lists, the first of which contains factors relating to the metal, the second to its environment. For simplicity we shall at the moment ignore the first list and deal with only two metals in definite states, *i.e.*, cast and turned zinc, and normalized mild-steel rod with mill scale removed and turned to a definite shape. The effect of mill scale requires a separate research; if left *in situ* it may be an important factor in determining the distribution of corrosion on different batches of steel; in fact, more important than small differences in chemical composition. As regards total amount of corrosion, however, the most interesting factor usually occurs in the second list.

The most important or controlling factor is that one which permits the slowest rate of corrosion; it will vary with the metal and the environment. It may be the operative electrode potential of the metal, as with Mg in NaCl solution, or the rate of oxygen supply, as with Zn and steel in the same solution.

Table II brings out the error contained in an idea that is still obstinately persistent, especially among engineers and metallurgists, namely, that each metal possesses an inherent property, called corrodibility, which can be ascertained once and for all and tabulated with other properties such as specific heat, conductivity, etc. All you chemists will see at once the fallacy, but I address myself, for a moment, to laymen.

The table shows that no such property can exist because corrosion is the result of the meeting of two reactants, the metal and its environment, and we find that it is often an environmental factor which determines the corrosion rate, especially with the industrially important metals.

TABLE II

Factors which influence corrosion rates in salt solutions

Metallic factors	Environment factors
(1) The electrode potential which is influenced by: State of aggregation; State of strain; Crystal orientation	(1) The temperature
	(2) The partial pressure of oxygen
	(3) The rate of supply of oxygen
(2) The hydrogen over-potential	(4) The concentration of H' ions
(3) Metals in solid solution	(5) The concentration of metal ions
(4) The presence of different phases	(6) The concentration and specific nature of other ions present
(5) The chemical reactivity	
(6) Surface condition	(7) The nature and distribution of corrosion products
	(8) The electrical conductivity of the solution

Environmental factors may exert their influence largely through the properties of metallic compounds. Let us take concrete examples. In conductivity water and oxygen, iron and steel are readily attacked and Zn and Mg less so, and we should list them in order of corrodibility as Fe, Mg, Zn.

In NaCl the order would be Mg, Zn, Fe.

In a strong alkali solution, Zn, Fe, Mg.

Thus not even a *relative* order of corrodibility can be given for a series of metals, and the word can only be strictly used for a specific metal in precisely defined conditions.

In measurements of corrosion on any one material the following physical factors must be considered:

(1) Preparation of the surface
(2) Method of suspension
(3) Size and shape of specimen
(4) Depth of immersion
(5) Cross section of vessel
(6) Volume of corroding liquid
(7) Stability of apparatus
(8) Temperature and particularly its fluctuations
(9) Pressure, particularly partial pressure of oxygen and its fluctuations

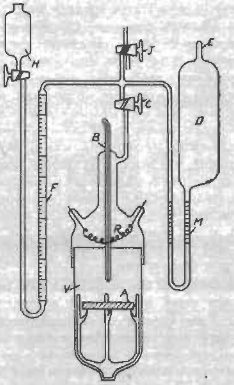


FIG. 2

Corrosion apparatus (diagrammatic)

Probably most chemists would be willing to guess, fairly confidently, how each of these factors would influence corrosion rates, but I expect to provide a surprise in the case of several of them, and it will soon become clear why comparable results are so hard to find in the literature.

The method of corrosion measurement which I shall first describe was designed for obtaining more accurate and fuller information than that usually required for the routine of a works laboratory. It is now known that zinc, iron, and mild steel corrode in salt solution and sea water by two mechanisms, namely, (1) the displacement of hydrogen gas, (2) oxygen depolarization. Reaction (1) sometimes causes a large proportion of the total corrosion (for instance, mild steel fully immersed in sea water beneath air may owe from 10% to 60% of corrosion to this mechanism, see Table VIII), but this

was only discovered when the ordinary loss-of-weight method of measuring corrosion in open beakers was replaced by measurements in a closed apparatus. The corrosion rate in our nearly neutral solutions may be controlled by the rate at which hydrogen gas can be disengaged, by the rate at which oxygen is supplied, or by the formation of obstructive films at anodes or cathodes. *Obviously any apparatus for studying corrosion quantitatively should provide for the periodic measurement of the oxygen absorbed and hydrogen evolved in the process, under controlled conditions of temperature and pressure.*

The principle on which our apparatus is based is shown in Fig. 2. It consists of a corrosion vessel, of 4·4 cm. diameter, which is connected on one side to an oxygen burette and on the other *D*, to a constant-pressure *bulb and manometer, and the whole can be placed in a* thermostat.

An experiment is started as follows:

(1) Place the metal disc in position on 3 glass points; seal up joint of vessel with vacuum wax. (2) Exhaust vessel and fill with oxygen. (3) Force in solution through capillary B; force out excess: depth of immersion and volume of liquid are thus controlled by position of end of capillary; seal off top of capillary. (4) Adjust pressure in bulb *D* to 760 mm. at 25°, and then that in corrosion vessel; seal off bulb and vessel capillaries. (5) *Close tap C on corrosion vessel and leave for 24 hours*: pressure falls owing to corrosion causing oxygen absorption: *hydrogen evolution may partly neutralize this.* (6) Open tap and readjust pressure to 760 mm. by means of oxygen from burette *F*; observe amount of oxygen used by reading burette: this is the *apparent* oxygen absorption. (7) Burn hydrogen; 2/3 of contraction = H, and this volume must be added to apparent oxygen to give true oxygen.

The sensitivity of the apparatus can be varied by adjusting the cross section and graduations on the manometer *M* and burette. *For small amounts of corrosion, e.g., with zinc in distilled water a 2-c.c. burette may be used, graduated in hundredths; for N/10 KCl a* 15-c.c. burette graduated in tenths is suitable.

Since it is often essential to carry on experiments for very long times, it is obvious that all the oxygen in the largest burette that could be accurately read would too soon be consumed (over a litre has been used in a single experiment): consequently the burette must be refilled during the progress of the experiment; for this a three-way tap *J* is fitted and first swept out to get rid of air by turning it in one direction; oxygen is then introduced into the burette by turning it in the other.

The Standardized Measurement

(1) *Preparation of the surface.*—A machined surface is preferable, in my opinion, to one emeried or polished because of the ease, rapidity, and uniformity of production, particularly at the edges, and because it is believed to be less contaminated and more reproducible; it has been found essential for good reproducibility with cast zinc, but with rolled mild steel the difference between the two types of surface is not so great. Precautions must be taken against access of oil to the metal surface during machining. Zinc should be annealed in argon after machining.

(2) *Method of suspension.*—Horizontal specimens are supported on 3 fine glass points, with the upper surface 1·5 cm. below the gas-liquid interface, and vertical specimens are bored and hung on a glass hook.

Now, for my first surprise: a vertical specimen of similar area to our standard horizontal specimen, if suspended with its top at the same depth as the top horizontal surface corrodes at a nearly similar rate—the reason for this will become apparent later.

(3) *Surface area and shape of specimen.*—It is useful to adopt a constant surface area for specimens. Since both cast and rolled metals are readily obtainable in round bars and most laboratories contain an accurate lathe we have adopted as our standard test piece a circular disc, 2·5 cm. in diameter and 0·6 cm. thick, *i.e.*, with an apparent area exposed to liquid of 14·9 sq. cm. The thickness allows relatively weak metals, like cast zinc, to be turned easily to shape, otherwise a thinner disc would have been chosen. If specimens are required for vertical suspension and partial immersion their overall dimensions are 5 cm. × 2 cm. × 0·4 cm., with 3 cm. actually immersed, so as to give an area similar to the standard disc; they are prepared on a milling machine, which does not give such a smooth and reproducible surface as the lathe.

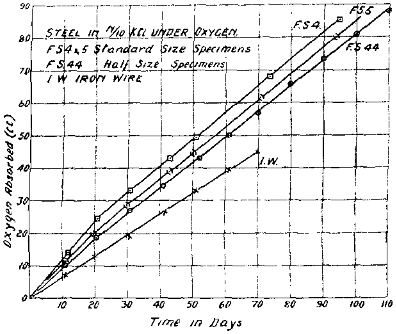


Fig. 3

An objection might be raised that the apparent area of a turned specimen is not the same as the true area, which must be greater owing to the presence of ridges and troughs. Any error is reduced as far as possible by giving a very fine last cut (on a precision lathe) which is reasonably reproducible; but the real answer is my second surprise for you. Fig. 3 shows the oxygen-absorption-time curves for four specimens, two of standard size, one of exactly half the area but made of the same steel bar, and one of approximately 1/9th of the area; the last was a piece of mild steel wire of nearly similar composition to the discs. It was bent round the glass points of the stand so as to be immersed at

approximately the same depth. Corrosion was carried out in N/10 KCl in standard conditions. The slopes of the corrosion-time curves corresponded to oxygen absorptions 0·84, 0·80, and 0·70 c.c. per day over straight line portions of the curves. It is clear that even a very small specimen can use almost the whole of the oxygen which reaches it in the standard thermostated vessel which is 4·4 cm. in diameter.

This result seemed to be due to the restriction of the rate of oxygen supply by the small cross section of the vessel so that even the small specimen could use the whole of it. To test this, a vessel with a 15-cm. diameter was substituted, and standard and half-sized specimens tested; the corrosion rates were again roughly similar and about 3·6 times that in the standard vessel—far faster than in an open 3-in. beaker on a laboratory bench.

It was not practicable to use a still larger diameter vessel with the standard apparatus, so simple loss of weight experiments were carried out in circular earthenware troughs 23·5 cm. in diameter exposed to laboratory air and temperature fluctuations. At the end of 20 days, the total weight losses of standard and half-sized specimens were as 1·7 : 1 or 70 and 41 mg. respectively, and at the end of 50 days as 1·75 : 1 or 153 and 87 mg., *i.e.*, still far from proportional to the areas. These weight losses are less than 50% greater than those given in the standard apparatus in the thermostat and actually much less than those in the 15-cm. diameter thermostated vessel (in both of which oxygen was used). Clearly the absolute rate of oxygen supply is not the only factor to be considered.

Table III

Relation of surface area to corrosion

N/10 KCl

Size of vessel: Diam., cm.	Cross section, sq. cm.	Loss of weight in 50 days, mg.: Standard size, 14·9 sq. cm.	Half size, 7·5 sq. cm.	Ratio. Standard size / half size
I 4·4 .... (standard size)	15·2	144·5	139	1·04
II 4·4	15·2	95	68·6	1·38
III 7·8	47·8	178	122·8	1·44
IV 12·8	128·7	205·6	129·5	1·58
V 20	314·2	185	112	1·65
VI 23·5 ..	433·7	153	87	1·75

I Thermostated (in oxygen); II to V Not thermostated, but under wooden cover (in air); VI Freely exposed (in air and N/2 NaCl)

Experiments were next carried out in circular glass vessels, 12·8 cm. and 7·8 cm. in diameter, freely exposed to the laboratory air, but protected from draughts by a wooden cover. The results are given in Table III. It is clear that abolition of thermostating and increase of size of vessel tend toward giving proportionality between area and total corrosion, but never achieve it with any convenient size of vessel in apparently stagnant conditions, even when quite small specimens are used. It is also clear that the presence of convection currents is a very important factor. If the currents were increased to such an extent that visible motion occurred, proportionality would probably be achieved.

(4) *Depth of immersion.*—Our standard depth for the top surface of the specimen is 1·5 cm. below the liquid surface. Fig. 4 shows the influence of depth on the rate of oxygen absorption by zinc and mild steel. The curve forms are similar and show the astonishing fact that between the 1·5 cm. and 10 cm. the depth has little effect on the corrosion rate. Heyn and Bauer have

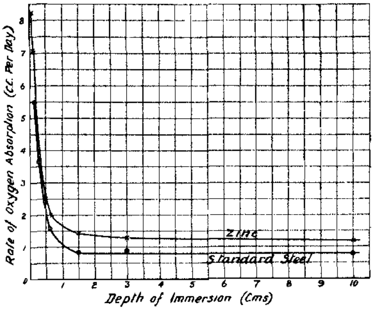


Fig. 4

found that the rate was nearly constant between an inch and two feet even in non-thermostated conditions. The curves have two main branches but are not rectangular hyperbolas; evidently the main supply of oxygen is not by diffusion except at very shallow depths. The form of the curves is probably due to the fact that the oxygen which produces most of the corrosion of both metals moves through the liquid by two different processes, diffusion and convection. At very shallow depths diffusion predominates; at the standard depths it can supply less than ⅓rd of the maximum oxygen

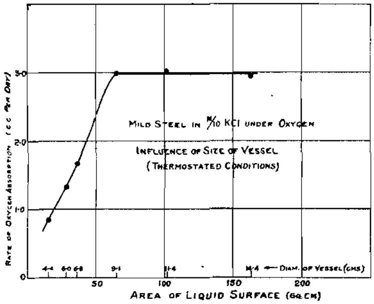


Fig. 5

Effect of cross-section of vessel on corrosion rate

supply permitted by the vessel, and convection predominates. Probably diffusion only operates effectively over a narrow zone near the metal surface and convection currents circulate elsewhere. When temperature and pressure are kept nearly constant, the convection

currents may be due partly to the movement of corrosion products, but mainly to a mechanism investigated in great detail by Wroblensky and Stefan, Hüfner and Tor Carlson. These investigators brought out much

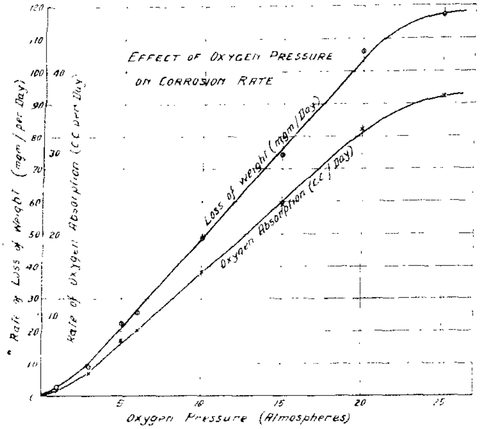


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FIG. 6

Effect of oxygen pressure on corrosion rate of steel

evidence to show that "oxygen streaming" takes place into the interior of thermostated liquids, the mechanism of which is not quite clear but may be due to surface absorption of oxygen causing an increase in the specific

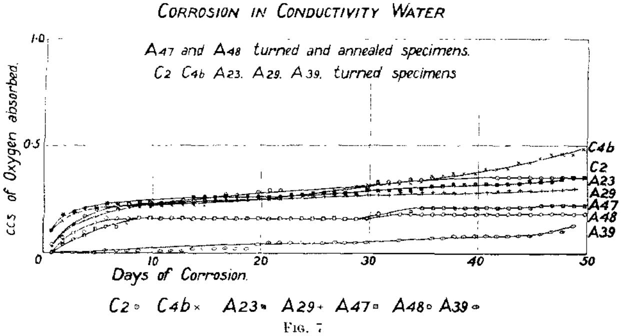


FIG. 7

Zinc in conductivity water

gravity of the surface layers, which consequently fall and convey oxygen to the interior.

If this be the true cause of the convection currents, they will specially direct oxygen towards the metal surface where it is used up by corrosion, and their maintenance will be dependent on the corrosion process itself, for the streaming will only take place if the layers of liquid near the metal are wholly or partially exhausted of oxygen. Near the gas-liquid interface, the actual amount of oxygen which this process can bring towards the metallic surface is probably small relatively to diffusion, but lower down even a small specimen can use all the oxygen supplied by "oxygen streaming" in normal conditions.

It is now clear that one kind of convection, which we may call "oxygen streaming," is specially directed to

the metal by the corrosion process itself. But quite another kind, wholly independent of the process, has been demonstrated by Adeney, whenever changes of temperature and pressure cause evaporation; this increases salt concentration and specific gravity in the surface layers of solutions which fall, carrying oxygen with them.

These Adeney convection currents will occur in non-thermostated open vessels and will not necessarily be concentrated towards the surface of the metal but will wander throughout the vessel; some that would reach a large specimen will miss a small one, and the large specimen will, therefore, corrode faster than the small one. In general, these Adeney currents will carry more oxygen and cause more corrosion than the Stefan-Carlson "streaming" and are, therefore, desirable if short experimental periods are essential, but they are not easy to produce in definite and constant strength; their use, therefore, lowers the reproducibility of corrosion experiments. On the other hand, thermostated experiments in closed vessels give relatively slow but readily reproducible corrosion rates. We shall return to this dilemma later.

A general rise or fall of the thermostat temperature will not usually affect all parts of the corrosion vessel quite uniformly and will thus give rise to a third, *i.e.*, a thermal type of convection current which is also rather difficult to reproduce. It has now, I think, become clear that a solution in which corrosion is taking place is never truly, but only apparently, stagnant.

(5) *Cross section of vessel.*—The influence of the cross section of the vessel on the corrosion rate throws further light on this matter. Increased cross section increases corrosion rate. Fig. 5 shows the relation between the two. With any given cross section there is a maximum possible corrosion rate which is determined probably by the rate at which oxygen can be transferred from the gas-liquid boundary to the metal surface; in the standard vessel it corresponds to an oxygen absorption of at least 1·5 c.c. a day when zinc is used. With a 9·1, 11·4- or 14·4-cm. vessel the rates are increased about 3·6 times, with both zinc and mild steel; this means that a considerable increase of oxygen supply does not alter the relative corrosion rates of the two metals—a very important conclusion since it shows that the rates of oxygen supply and not the basic potentials of the metals control the corrosion rates. The rate of hydrogen evolution does not alter with increase of cross section of the vessel in spite of the fact that the oxygen supply is greatly increased, and might be expected to cut down the rate. It seems to be dependent upon overvoltage, the basic potential of the metal and, of course, the hydrogen ion concentration.

(6) *Volume of liquid used.*—In our standard vessel this is 100 c.c.; in the larger vessels 500 c.c. The volume (as distinct from cross section) is an important factor if the composition of the liquid is altered by the corrosion process. With zinc in dilute KCl solutions increase of alkalinity occurs as corrosion proceeds; it is caused by transference of chlorine from the solution to the corrosion products; the effect on the corrosion rate in N/10 KCl, for instance, becomes pronounced after about 100—110 days in a 100-c.c. vessel, and the process may be brought almost to a standstill in about 145 days (see Fig. 11). With mild steel no such effect is apparent before at least 600 days.

(7) *Stability of apparatus.*—The necessity for stability of apparatus arises from the fact that oxygen is conveyed about the corrosive liquid by means of convection currents which are notably increased by even slight vibration. Tests for stability should be made by the sensitive mercury horizon method. When thermostats are used it is essential to support the motors, stirrers, and all other moving parts independently of the thermostats themselves so as to avoid transmitting motion.

(8) *Temperature.*—Our standard temperature is 25° C., which is much more easy to keep constant than 20° C. Few accurate data on temperature coefficients have been published. Evans and Hoar give three measurements at 0°, 20°, and 30° for the corrosion of partially-immersed

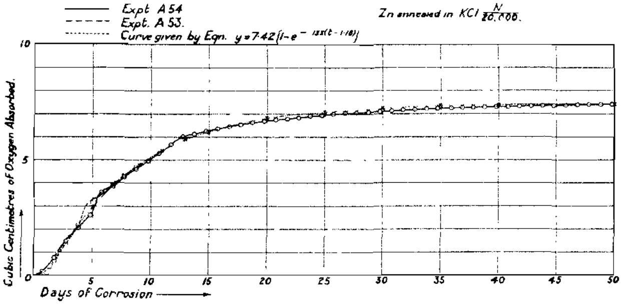


FIG. 8

Experimental and theoretical curves in N/20,000 KCl

pure sheet iron in 2·5 N KCl ; from these it appears that the coefficient is low, and not unlike that characteristic of surface reactions. Nevertheless, fluctuations of temperature are very important because they give rise to convection currents which increase the oxygen supply and so give increased rates whether the fluctuations are up or down from the selected temperature. This fact can be utilized to ascertain whether the corrosion rate *in a given experiment is controlled by the rate of oxygen supply* ; if it is, an artificially induced temperature fluctuation will increase the corrosion rate.

In practice it is sufficient to keep temperature-control within the limits of $\pm 0{\cdot}05°$ C.

(9) *Oxygen pressure.*—Twenty-five years ago Walker, Cederholm, and Bent showed that the rate of corrosion of iron wire in distilled water was proportional to the partial pressure of oxygen up to one atmosphere in oxygen and nitrogen mixtures. Recently Chaudron worked with oxygen pressures up to 120 atmospheres and showed that steel in NaCl does not become passive but corrodes more rapidly as the pressure increases ; his curve is not linear and actually indicates considerable corrosion at zero oxygen pressure. This is unexpected from the work of Walker, Friend, Lambert, and others. Lee, working simultaneously and independently at Teddington, found the curve for N/10 KCl, shown in Fig. 6.

It cannot be assumed that a curve similar to that for KCl would be found in other salt solutions : with sea-water, for instance, increase of oxygen pressure has a much smaller effect in pushing up the corrosion rate. It has been found that the rate of hydrogen gas evolution is largely independent of the oxygen partial pressure between the limits $\frac{1}{5}$ atmosphere and 3 atmospheres of oxygen. Though the absolute rate is not much altered, the proportion of the total corrosion due to hydrogen evolution is greatly changed.

Typical corrosion-time curves of zinc and mild steel.—In order to obtain time-corrosion curves in the defined conditions stated, special precautions were taken as regards chemical purity. A preliminary research was made to ensure ample supplies of high grade conductivity water. Two stills are used, and each will yield about 7 litres a day of water which has a conductivity less than $0{\cdot}1 \times 10^{-6}$ inverse ohms ; for special purposes, water as good as $0{\cdot}045 \times 10^{-6}$ has been obtained. Clear silica or resistance glass is used for the corrosion vessels. The oxygen or air used as atmosphere is purified in the usual way. The use of oxygen will be assumed except when the contrary is stated.

A. *Zinc.*—Some curves in conductivity water for special Australian electrolytic zinc are shown in Fig. 7. The total corrosion at the end of 50 days is less than 1 mgm. The curves in N/100,000 and N/20,000 KCl (see Fig. 8) have been found experimentally to be exponential in form. The chlorine gradually disappears from the solution, but is found in the white precipitated corrosion products ; thus at any instant the total corrosion that has already occurred determines the concentration of chloride left in the solution, and this, in turn, determines the corrosion rate.

If the concentration of chlorine in solution be the controlling factor, we should expect that the corrosion rate would be unaffected by changes in the rate of oxygen supply, and this was found to be so for solutions up to about N/5000 KCl, but the curve for N/1000 shows a short linear branch for several days, which lies below the possible exponential curve (see Fig. 9). This linear branch was controlled by the oxygen supply, for if this

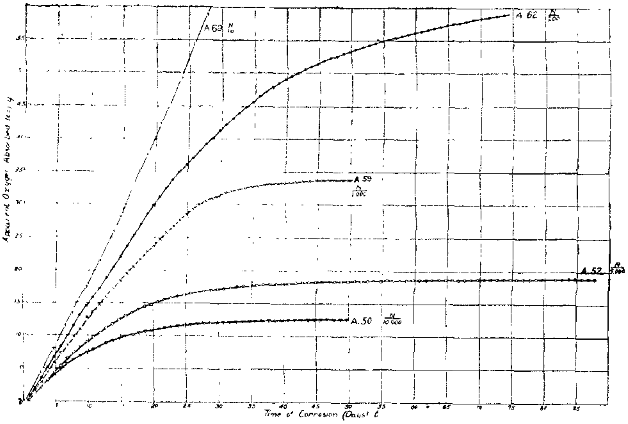


Fig. 9

Typical curves for zinc in different concentrations of KCl

was increased the slope increased. In very weak solutions the corrosion due to hydrogen evolution is small enough to be neglected, but you will notice in Fig. 10 three curves given for one specimen in N/5000 KCl. The apparent oxygen curve is obtained experimentally, also a hydrogen evolution curve; from these two the true oxygen and total corrosion curves are obtained. In solutions still stronger than N/1000 the linear portion of the oxygen absorption curve in a standard vessel *becomes prolonged, as shown in Fig. 11* for N/10 KCl.

These curves have historical interest as being, I believe, the first complete set ever published for any of the metals, such as Al, Zn, Fe, and steel, which corrode both by oxygen absorption and hydrogen evolution. The oxygen absorption curve as a whole is raised a little above its true position owing to slight vibration of the apparatus which was unnoticed in the early stages of the experiment. The hydrogen curve shows an "induction period" which is rather prolonged, since the total metallic impurity in the sample of zinc was only 0·02%.

"Spectroscopically pure" zinc causes much less hydrogen evolution than ordinary "commercially pure" zinc, but the oxygen absorption rate is quite similar, if allowance be made for the effect of the H. One part of metallic impurity in 10,000 is sufficient to raise greatly the rate of hydrogen evolution of nearly pure zinc. Fig. 12 shows a set of hydrogen evolution curves for strong KCl solutions and *Figs. 13* and *14* the variation of corrosion rate with salt concentrations and with oxygen solubility, the latter indicates the completeness of oxygen control. Fig. 15 shows the degree of reproducibility ordinarily reached with zinc by the methods described above, and Table IV gives a comparison between the losses *of weight of the metal* at the end of several experiments and the results calculated from oxygen and hydrogen measurements.

B. *Mild steel.*—The "standard" metal ordinarily used was rolled mild steel prepared at the Vickers Works, Sheffield, by Mr. J. H. S. Dickenson; all details of manufacture have been recorded and it is denoted by the letters FS in the diagrams and tables, other materials used were highly purified iron prepared at the N.P.L. by electrodeposition and subsequent remelting *in vacuo*, and an ordinary sample of mild steel taken from a workshop stock. The analyses of all three are given in Table V.

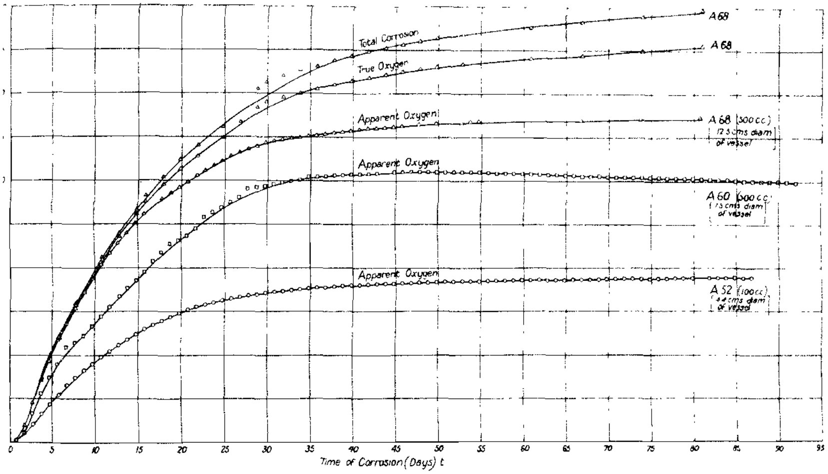


Fig. 10

Effect of cross-section of vessel on corrosion of zinc in N/5000 KCl

The experimental conditions were similar to those used for zinc. Hydrogen gas was evolved in all the experiments and some of the oxygen absorbed was, of course, used in the oxidation of ferrous to ferric iron. Consequently calculations of the amount of corrosion must be made from observations not only of hydrogen evolved and oxygen absorbed, but also from analyses of corrosion products made at the end of experiments. Since the proportion of ferrous to ferric iron changes with time a collection of analyses must be made, such as those shown in Fig. 16.

In order to make quite clear the method of calculation, *Table VI has been prepared; it gives an extract from* the laboratory notebook, and the procedure is as follows:

Table IV (*By courtesy of the Royal Society*)

Comparison between two methods of measuring corrosion

1	2	3	4	5	6
Specimen No.	Corroding liquid	Zinc by oxygen absorption, mg.	Zinc by loss of weight (corrected) mg.	Mean value of zinc corroded	Percentage variation of columns 3 and 4 from mean
A 93	KCl, N/2	2059·9	2029·71	2044·8	0·74
A 94	KCl, N/5	655·0	657·72	656·4	0·2
A 95	KCl, N/50	489·7	481·53	485·6	0·8
A 96	KCl, N/10	1578·9	1582·33	1580·6	0·1
A 97	K_2SO_4, N	541·6	546·21	543·9	0·4
A 98	K_2SO_4, N/10	1050·5	1022·28	1036·4	1·36
A 99	K_2SO_4, N/50	821·1	790·17	805·7	1·9
A 100	K_2SO_4, N/10,000	25·7	24·00	24·9	3·4
A 101	K_2SO_4, N/200	315·1	314·13	314·6	0·2
A 102	K_2SO_4, N/5	591·1	592·06	591·6	0·1
A 103	KCl, N/5	691·7	703·46	697·6	0·9
A 104	K_2SO_4, N/10	450·8	451·54	451·2	0·1

First: The "apparent" oxygen absorption is observed (columns 5 and 6 of Table VI); this is less than the true absorption because hydrogen has been evolved.

Table V

Analyses of mild steel and iron

	Mild steel FS	Commercial mild steel F	Purified iron FP
Carbon	0·13	0·11	0·018
Silicon	0·15	0·07	0·003
Sulphur	0·034	0·037	0·0015
Phosphorus	0·034	0·030	0·003
Manganese	0·46	0·56	trace
Nickel	*0·20*	*nil*	*nil*
Chromium	0·04	nil	nil
Copper	0·05	-	nil
Oxygen	0·02	-	0·071

Secondly: Hydrogen evolution is measured by burning. This enables the true oxygen absorption to be determined: also the corrosion due to hydrogen evolution (columns 11 and 10 of Table VI).

Thirdly: The "equivalent oxygen absorption" (last column of Table VI) is obtained from the true oxygen absorption plus half the hydrogen evolution.

Fourthly: This value (in c.c.) is introduced in the equation given below Table VI: the percentage of ferrous iron in the corrosion product is also introduced, and the result is corrosion expressed in terms of oxygen, assuming the iron to be divalent. A factor is then used to convert the value obtained from the equation into grms. of metal corroded. This value is then checked by a loss of weight measurement made at the end of the experiment.

Note.—Column 8 is obtained from columns 7 and 4 corrected for the time (1 hour) which elapsed between the oxygen and hydrogen readings: the correction is one twenty-fourth of column 5. The figure + 0·03 in column 5 is a correction for the amount of oxygen absorbed during the one hour occupied by hydrogen *burning, cooling, etc.*

A picture of reproducibility is given in Fig. 17. It will be noticed that in the more dilute solution the reproducibility of oxygen absorption is very good for about 60 days, and then falls off. In N/10 it is quite good up to 250 days or so. The total corrosion, expressed as oxygen used can be obtained from the experimental

Table VI

Results of oxygen absorption and hydrogen evolution measurements

Mild steel

1	2	3	4	5	6	7	8	9	10	11	12
Dates	Days of corrosion	1st reading	2nd reading	Diff. (apparent O)	Total apparent oxygen used	Reading after H burning	Contraction (corrected)	H evolved	Total H	True O	H/2 + O as oxygen
April 8	42·7	2·84	3·71	0·87	40·63	4·75 (1 hr.)	1·01	0·67	2·28	42·91	44·05
,, 10	44·7	4·75	6·18	1·43 + 0·03	42·09						
,, 12	46·7	6·18	7·73	1·55	43·64						
,, 14	48·7	7·73	9·23	1·50	45·14						
,, 16	50·7	9·23	10·82	1·59	46·73	11·49 (1 hr.)	0·64	0·43	2·71	49·44	50·80

The *total corrosion in terms of oxygen* is obtained from the formula:

$$V = \frac{T}{1{\cdot}5 - \frac{p}{2}}$$

Where V = total corrosion expressed as c.c. of oxygen.
T = last column of table.
p = fraction of total iron in the corrosion products found in the ferrous state.
To convert to mg. of iron corroded, multiply V by the factor 4·568.

curves and is also good, as shown in the Table VII, which gives the slopes of the linear parts of the curves. Note that two different kinds of mild steel and one sample of highly-purified iron give closely similar results in the same solution, and that the rate is, for a long time, higher in the more dilute solution, a point we shall deal with shortly.

curves were determined to some extent by the rate of oxygen supply in the early stages of the experiment; this was surprising, because the conductivity of the water used in the experiments was only $0{\cdot}07 \times 10^{-6}$ inverse ohms, and might have been expected to limit the rate severely.

The exponential forms of the curves were found to be

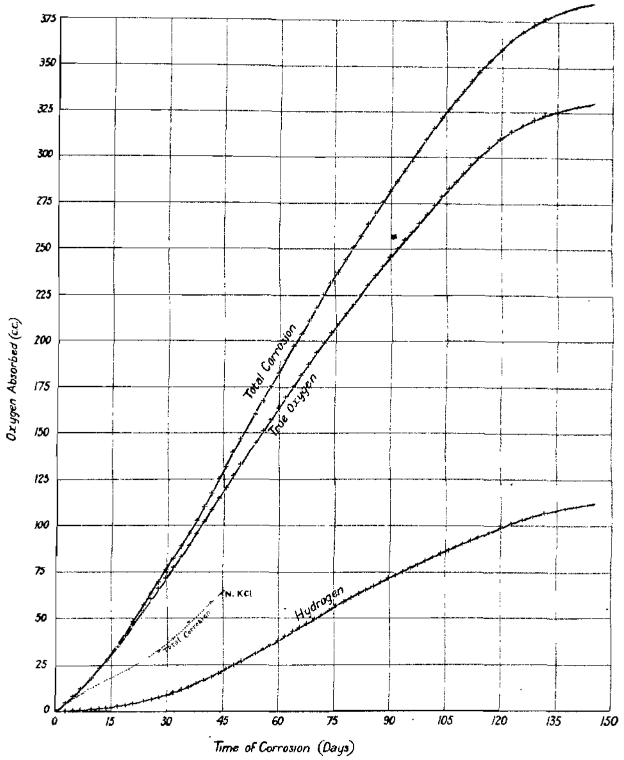


FIG. 11

Curves for zinc in N/10 KCl

In conductivity water and oxygen, purified iron and mild steel corrode at easily measurable rates, and much faster and longer than zinc. Fig. 18 shows that the curves for standard steel are exponential in form: similar forms have been obtained for pure iron and a random sample of commercial mild steel taken from a workshop stock. It was found that the slopes of the

connected with the formation of mounds of corrosion product over part of the surface of the metal. These generally took the form of congeries of cones or flat discs which had gradually narrowing openings. If it be assumed that the corrosion rates were determined by the sizes of these openings, a curve of exponential form would be expected on mathematical grounds; the

assumption was based on the facts that corrosion ceased with the complete closing over of the mounds, but was *maintained* in experiments in which they did not close.

Somewhat similar results were obtained in the N/100,000 and N/10,000 KCl corrosion/time curves for the latter correspond to oxygen absorption curves

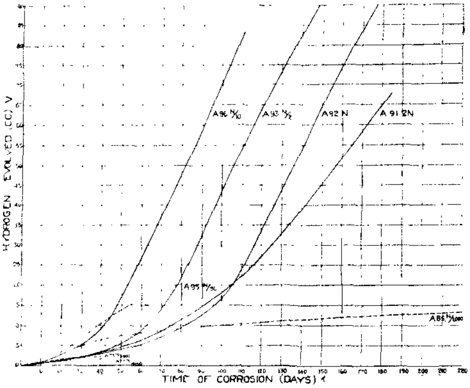


FIG. 12

Hydrogen gas curves. Zn in KCl solutions

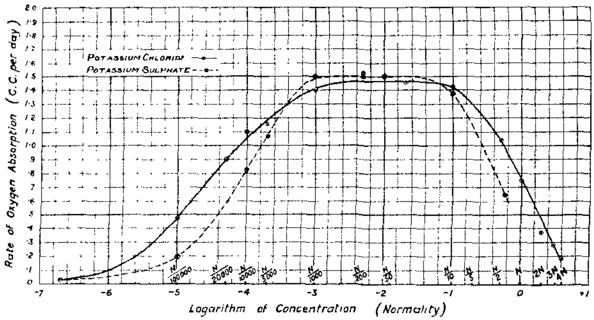


FIG. 13

Variation of corrosion rate of zinc with concentration of salt

TABLE VII

Corrosion rates (in terms of oxygen absorbed per day)

N/10,000 KCl		N/10 KCl	
Specimen	Rate per day	Rate per day	Specimen
F12	0·99	0·57	F4
F11	0·99	0·55	F6
FS2	1·06	0·60	FS4
FS3	1·06	0·59	FS5
FP3	0·84	0·59	FP1
FP4	0·70	0·58	FP2

Note.—The rates are taken from the initial, nearly linear slopes for N/10,000, and from the second, persistent, linear slope for N/10 KCl.

shown in Fig. 19 and were found to be hyperbolic tangents (up to point A)—a form that would be expected if the mounds of corrosion product were hemispherical. Further observations showed that the fall in corrosion rates indicated by the curves was not due to diminution of chlorine ions in solution (as occurred with zinc), nor to any changes at, or reduction in size of, unattacked areas. The mounds became less conspicuous as the concentration of KCl increased; they were still noticeable in N/1000 but absent in N/10; and were not formed in any solution when air was substituted for oxygen.

The fact that they exercised a controlling influence on corrosion rates was shown by removing them during the course of experiment. The result of removal is to restore the corrosion rate to its original value, as shown by Fig. 19, beyond point A. Final divergence between the two curves is due to the closing up of the new corrosion mounds at slightly different rates.

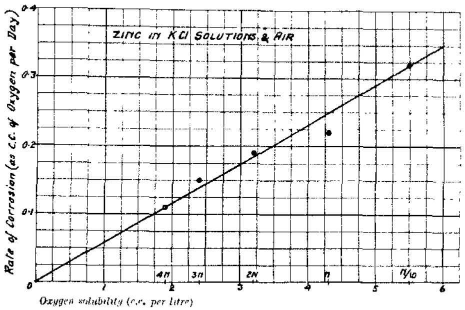


FIG. 14

Variation of corrosion rate with oxygen solubility

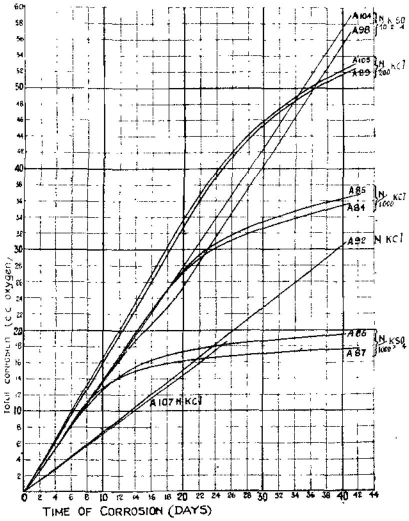


FIG. 15

Curves showing degree of reproducibility

Curves for steel in N/10 are shown in Fig. 17. They are linear up to about 250 days, except for a slight bend at the end of 20 to 30 days. The slopes are dependent on the rate of oxygen supply, for temperature fluctuations give increased slopes. A notable feature of the curves for N/10 KCl is their lower slope as compared with N/10,000 : this occurs with purified iron as well as steel. The slopes are also lower than the slope of zinc in a similar solution, although in conductivity water and dilute solutions the steel curves lie above the zinc curves. Evidently some factor is preventing the steel from taking full advantage of the maximum oxygen supply allowed by the experimental conditions. I shall return to this point shortly.

In still stronger solutions the oxygen absorption curves are practically linear. The slopes of the linear branches have been plotted against KCl concentration in Fig. 20. For weak solutions in which the curves were not linear, the slopes of tangents to the initial parts of the curves have been used. The oxygen-absorption/concentration curve consists of four branches : (1) The first extends up to N/100,000 and is controlled, apparently, by the concentration, but not necessarily by the conductivity of the solution ; the *area* of attack increases. (2) The second branch extends from N/100,000 to N/5000, and is controlled up to a certain limit by the oxygen supply which is itself dictated by the dimensions of the vessel and other experimental conditions. (3) The third branch covers N/5000 to N/200. In this range the nature of the corrosion products and the slopes of curves are variable and may change in the course of a single experiment—the mounds characteristic of weak solutions tend to disappear. (4) The fourth branch extends from N/200 to 4N and is controlled by the rate of oxygen supply, which is, in turn, controlled by the oxygen solubility in this region ; it is, nevertheless, suppressed below the second branch even when the fall in solubility is negligible. Fig. 21 shows the relation between rate of corrosion and oxygen solubility. With higher rates of oxygen supply this branch would be

raised above the second branch, which is but relatively *slightly affected by increase of oxygen supplies.*

I have already mentioned that the curves in solutions of N/10 and upwards remain linear for long periods.

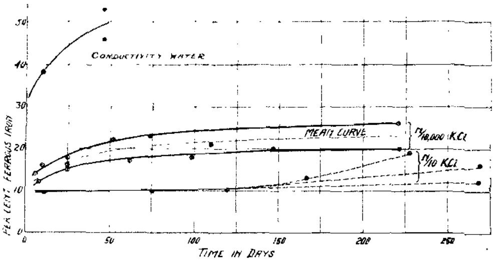
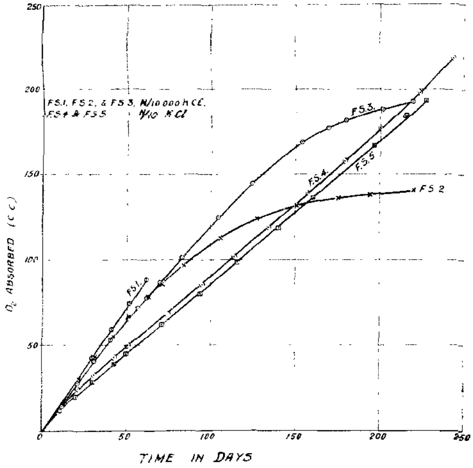


Fig. 16

Per cent. ferrous curves

In a few experiments that have been carried on for more than a year or with specially high corrosion rates obtained by the use of wide vessels, the slopes actually



By courtesy of the Royal Society

Fig. 17

Oxygen absorption curves of steel in N/10,000 and N/10 KCl

increased with time, as shown in Fig. 22; yet the specimens became covered with rust to such an extent that *no metal at all could be seen. This rust consisted* mainly of a lower black layer which was closely similar *to the mineral magnetite,* and an upper layer of brown ferric oxide in the gamma, magnetic, form. Evidently accumulations of these substances have no appreciable restrictive effect on the rate of oxygen absorption by corrosion up to 600 days or so. The contrary assumption is frequently made and an explanation of the phenomenon of "pitting" on steel is often based on it. This explanation is as follows: since less oxygen will reach *the metal beneath rust deposits than elsewhere, the*

...sulting differential aëration will set up a potential difference and cause local corrosion at the least aërated part of the metal situated beneath the rust. It seems, however, that rust is a result rather than a cause of ...ing, which is readily explainable on quite other ... and will be discussed in detail later. Up to about

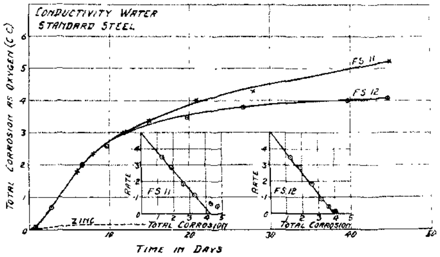


Fig. 18

Corrosion/time curves. Conductivity water

... days the rust was loose and could be easily shaken off the metal, without any result on the corrosion rate. Later, however, it formed a hard crust which could not be shaken off. *The corrosion rate then fell, as shown in* Fig. 22. This may have been due to the decreased

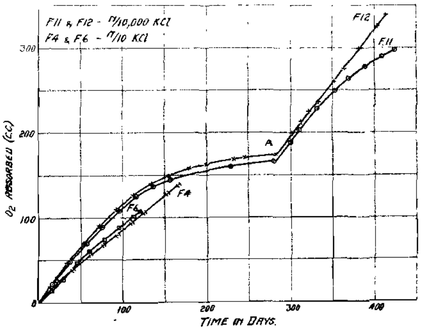


Fig. 19

Oxygen/time curves in N/10 and N/10,000 KCl

ability of ions to pass out through the crust, and of oxygen to pass in, so that anodic polarization occurred.

Mention has been made of the low slope of the curve in N/10 KCl which is below that in N/10,000, and that of zinc in N/10 as shown in Fig. 22, though all appear to be controlled by the rate of oxygen supply, and inquiry may be made how this can be, since the experimental conditions are identical.

Oxygen control can be regarded as operating either at cathodes or anodes, or both. Cathodic control operates through the depolarization of hydrogen, but anodic control, perhaps, through the oxidation of an ion-proof film of ferrous hydroxide, precipitated from its saturated solution. Its solubility corresponds to four parts per 1,000,000 of iron at a p_H value of 7, and becomes less with increase of alkalinity—about 0·1 at p_H 11, according to Whitman, Russell, and Davis. Oxidation *of ferrous hydroxide in presence of relatively high* alkalinity, at smooth or very slightly attacked metal *surfaces, gives a uniform protective layer of ferric* oxide which can only be broken down in special conditions. Partial oxidation in neutral or only slightly alkaline conditions, at a surface roughened by corrosion or other means, may result in a heterogeneous film, pervious to ions, which allows corrosion to proceed slowly. On this view the presence of oxygen at an anode is necessary for the corrosion of iron to proceed,

though the amount required may be small, especially in presence of chlorides. With zinc, oxygen is not necessary at an anode because its hydroxide does not prevent the passage of zinc into the solution in relatively concentrated KCl, except in the presence of high alkalinity, and even then only temporarily.

The high corrosion rate of iron relatively to zinc in conductivity water and very weak KCl solutions may be due to the depression of the rate of zinc dissolution by absence, or the observed rapid diminution, of Cl ions *without which a precipitated protective film of hydroxide is formed*; with iron the concentration of Cl ions is not diminished by the *corrosion process, nor is* their presence necessary for a moderate corrosion rate, since oxygen alone can destroy the protective effect of the ferrous film except in presence of excess alkali.

At this point some horrid sceptic is probably saying to himself: All very nice, but he hasn't yet explained why the corrosion rate in N/10,000 KCl is greater than in N/10 at any rate for 100 days. I propose therefore to take the line of the prisoner in the dock who remarked: "Since all is discovered I will now confess everything." The truth is that the explanation is not certain, though I think some reasonable suggestions can be made.

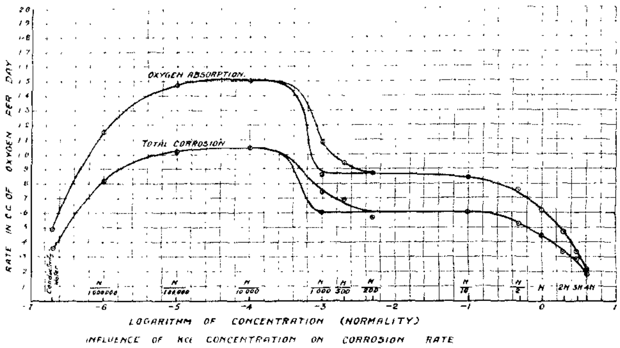


FIG. 20

Rate of corrosion of steel—log. conc. KCl

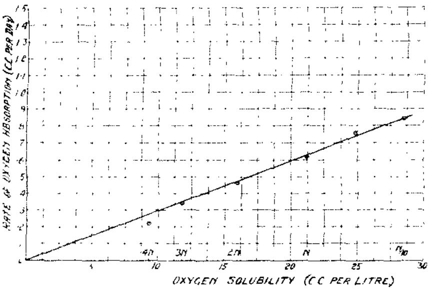


FIG. 21

Rate of oxygen absorption by steel—oxygen solubility

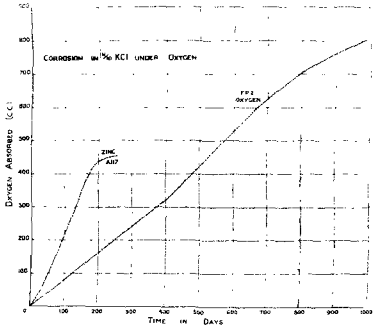


FIG. 22

It was found that for a short initial period the corrosion rate is actually greater in the stronger solution, and that during this period the curve is parabolic. The parabola soon fades out into a straight line which lies below the curve characteristic of the weaker solution for more than 100 days—*i.e.*, until the "mounds" cause appreciable diminution of corrosion rate.

(*To be continued.*)

SOME EFFECTS OF THE ADDITION OF TELLURIUM TO LEAD*

By W. SINGLETON and BRINLEY JONES

In the course of an investigation of the effect of the addition of small amounts of other metals to lead and lead alloys, it has been found that lead to which a small amount of tellurium has been added shows an increased resistance to corrosion. As judged by the flash test in the British Standard Specification for chemical lead, lead containing tellurium in amounts of the order of 0·07—0·10% does not "flash," and will in fact withstand, for short periods, the action of boiling concentrated sulphuric acid—properties not possessed by any other type of lead or lead alloy. This increased resistance to attack by sulphuric acid has been substantiated by actual exposure tests in a sulphuric acid plant where the loss in weight of the tellurium-lead, when exposed at the same time and in the same conditions, was only one-seventh of that of the most resistant chemical lead hitherto known.

It is proposed to discuss in this paper in some detail another most important aspect of tellurium-lead, viz., the physical properties.

The addition of tellurium to lead markedly affects the physical properties, as is shown below. For convenience, *the results of the investigation are divided into* the two following main sections:

A. Rolled sheet

B. Extruded products.

Tensile, fatigue, and freezing tests are described in the appropriate sections. With the exception of the

TABLE I

Tensile tests on rolled sheets. "Rapid" rate of straining

Type	Ultimate stress after 2 hr., lb./in.²	Ultimate stress after 12 days, lb./in.²
Lead + 0·02% tellurium .	3874	3814
Lead + 0·043% ,, .	4988	4577
Lead + 0·066% ,, .	4933	4068
Lead + 0·085% ,, .	4580	3793
Chemical lead sheet ..	—	2150
Lead + 0·06% *copper* ..	—	2520
Lead + 8% antimony ...	—	4500

est results shown in Table I, all other tensile tests were arried out on specimens 12 in. long, 1·5 in. wide, and ·125 in. thick, with a gauge-length of 8 in. Unless therwise stated, two speeds of straining were used, iz., "Rapid"—speed of straining 2 in. per minute; "Slow"—speed of straining $\frac{3}{32}$ in. per minute.

* Paper read before the Institute of Metals on March 8 and published by permission of the Institute.

A. ROLLED SHEET

The results given in Table I are averages of a number of closely agreeing values obtained from ingots of tellurium-lead, *cold-rolled from* $\frac{3}{4}$ *in. to* $\frac{1}{16}$ *in. in thickness,* and tested in tension (*a*) within 2 hr. of, and (*b*) 12 days after, rolling. These results are compared with chemical lead sheet, *copper-lead, and* 8% *antimonial lead. All* the samples were stored at room temperature.

The abnormal values for tensile strength, together *with the general behaviour of the test-pieces, indicate* that all the samples of rolled lead containing more than 0·02% of tellurium are in a highly cold-worked state. This is borne out by photomicrographs of sections of the rolled tellurium lead sheet, which show structures having the general characteristics associated with the cold-worked state and demonstrate that tellurium raises the temperature of recrystallization in lead. Figs. 1 and 3 (Plate I) show sections of freshly-rolled sheet in which the crystals are elongated and deformed, whereas in ordinary rolled lead sheet recrystallization is rapidly completed at ordinary temperatures; sections from such a material are shown in Figs. 2 and 4 (Plate I).

Ingots 2 in. thick (tellurium contents approximately 0·02—0·10%), and weighing 20 lb. each, were rolled to $\frac{1}{8}$ in. in thickness. Rolling was commenced at a temperature of about 100° C., the final reductions being carried out cold. The results of tensile tests, carried out after 1 day and subsequently at various periods, to determine the effect of time, are given in Table II. The samples were stored at room temperature.

The gradual reduction in strength in the specimens containing less than 0·06% tellurium indicates that annealing proceeds slowly with time, and in these cases recrystallization is not entirely prevented. The structure tends to change into a mass of minute crystals immediately after rolling, and eventually reaches a stable condition.

Fig. 6 (Plate I) shows the fine-grained structure of an aged cold-rolled tellurium-lead sheet which has lost some of the strength resulting from cold-work and has become more ductile. Fig. 5 (Plate I) shows incipient recrystallization in a freshly-rolled sample. It would appear *from these results that the effect of tellurium is complete* at 0·05—0·06%. It is important to note that the effects of cold-work on tellurium–lead result in toughening rather than in the brittleness usually associated with severely cold-worked metals. Large ingots can be cold-rolled quickly with no sign of cracking, and the rolled material may be bent double immediately and

TABLE II

The effect of ageing at room temperature on the tensile strength of rolled tellurium–lead sheet. "Rapid" rate of straining

Lead containing:	0·02% tellurium		0·04% tellurium		0·06% tellurium		0·10% tellurium	
	Ultimate stress, lb./in.²	Elongation, % on 8 in.	Ultimate stress, lb./in.²	Elongation, % on 8 in.	Ultimate stress, lb./in.²	Elongation, % on 8 in.	Ultimate stress, lb./in.²	Elongation, % on 8 in.
After 1 day	4037	12·0	4498	14·0	4037	7·8	3946	15·1
After 6 days	3937	19·6	4252	13·3	3831	17·2	4107	14·5
After 10 days	4005	22·7	4215	19·0	4197	15·6	3883	12·2
After 20 days	3836	17·6	3846	25·0	4189	14·4	3892	12·5
After 45 days	3520	23·1	3648	23·4	4110	17·0	4022	14·0
After 90 days	3230	27·0	3266	30·0	3798	23·0	4022	14·0
After 140 days	3173	28·1	3140	31·7	3739	16·1	3916	23·0

hammered flat without cracking. Cold-rolled tellurium-lead sheet can be annealed at higher temperatures, as shown in Table III.

TABLE III

Annealing of tellurium-lead. "Rapid" rate of straining

Material	Treatment	Ultimate stress, lb./in.^{2}	Elongation, % on 8 in.
Lead + 0·06% tellurium	1 day after rolling	4037	7·8
Lead + 0·06% ,,	2 hr. at 150° C.	3340	31
Lead + 0·06% ,,	1 hr. at 250° C.	2793	36

After annealing at 250° C. (Fig. 9, Plate II) the microstructure of the cold-rolled tellurium-lead shows that recrystallization has taken place, but without the development of coarse grains. For comparison Fig. 10 (Plate II) shows the structure of a sample of lead after annealing at 150° C. The foregoing results show that by addition of tellurium to lead in amounts up to 0·10% and the adjustment of rolling conditions, ageing, and heat-treatment, it is possible to produce metal containing not less than 99·9% of lead with a range of tensile strength from 2600 to 4000 lb./in.^{2} which is sensitive to cold-work under further strain. The much-increased resistance to corrosion combined with mechanical strength shown by tellurium-lead is of considerable importance in many industries where chemical lead sheet, although mechanically weak, is used because of its resistance to corrosion.

B. EXTRUDED PRODUCTS

Lead products are normally extruded hot and at temperatures above that at which recrystallization occurs in tellurium-lead, so that tellurium-lead produced by extrusion is in the fully-softened condition. Fig. 7 (Plate II) is a section from extruded tellurium-lead, and shows an undistorted and refined crystalline structure, which is remarkable when compared with a typical sample of extruded ordinary lead as shown in Fig. 8 (Plate II). Ordinary lead lacks toughness owing to recrystallization which takes place at room temperatures. Tellurium-lead should possess markedly increased toughness in the extruded condition, on account of its higher temperature of recrystallization.

Table IV gives the results of tensile tests carried out at the "rapid" rate of straining. The results are representative of a large number of closely-agreeing values for tensile tests. Tellurium-lead is slightly stiffer than lead in working and manipulation. When removed from the testing machine, the fractured ordinary lead test-pieces, although stiff at first, soften considerably within a short time, whereas those of tellurium-lead remain permanently stiff.

TABLE IV

Tensile tests on lead and tellurium-lead. "Rapid" rate of straining

Material	Ultimate stress, lb./in.^{2}	Elongation, % on 8 in.
Lead + 0·05% tellurium ..	2650—2900	55—67
Lead	2000—2400	30—65

Tellurium-lead responds to stress in a way unusual for lead alloys, and tensile tests carried out at slower rates of straining give evidence of its unusual physical properties, as is shown in Table V, in which the figures are representative of a large number of closely-agreeing values obtained from tests carried out at "slow" rates of straining.

TABLE V

Tensile tests on tellurium-lead and lead. "Slow" rate of straining

Material	Ultimate stress, lb./in.^{2}	Elongation, % on 8 in.
Lead + 0·05—0·06% tellurium	2300—2450	85—100
Lead	1630—1950	20—65

It is difficult to quote representative figures for lead owing to the considerable variations in grain-size in the material as found in commerce, and the above figures represent a wide range of samples obtaining in practice. The character of the elongation, as well as the degree of elongation, of the tellurium-lead is unusual. The test-pieces elongate in such a way that the distribution of strain remains uniform for a longer period than has hitherto been observed with lead or lead alloys. Local "necking" begins only long after that condition of strain or elongation, when other materials would have collapsed. Some idea of the unusual distortion occurring before fracture, and the uniformity of its nature, may be gathered from the simple analysis, given in Table VI, of the elongation of a typical test-piece of tellurium-lead, the gauge-length of which has been marked in inches. Corresponding figures are also given for a sample of chemical lead. The elongations on the two extreme 2-in. gauge-lengths of the tellurium-lead test-piece are 75% and 71% respectively, and on the lead 25% in each case. In the tellurium-lead, transition from uniformly distributed to local elongation is so gradual that no well-defined neck appears until an elongation of 70% is exceeded.

TABLE VI

Analysis of elongation of tellurium-lead and lead

	Tellurium-lead	Lead
Elongation on 2 in.%	144	118
,, 4 in.%	112	81
,, 6 in.%	100	64
,, 8 in.%	94	53

These results suggested that stress-strain diagrams taken from slow tensile tests should further differentiate between the physical properties of lead and of tellurium-lead. Through the kindness of Prof. B. P. Haigh, M.B.E., D.Sc., Professor of Applied Mechanics at the Royal Naval College, Greenwich, tests were carried out on a Denison variable-speed machine at a rate of straining of 0·018 in. per minute. The stress-strain curves are shown in Fig. 11, and the results are given in Table VII.

TABLE VII

Tensile tests on lead and tellurium-lead. Rate of straining—0·018 in. per minute

Material	Ultimate stress, lb./in.^{2}	Elongation, % on 8 in.
Lead + 0·05% tellurium	2081	92·4
Lead	1373	51·3

The rate of straining was twice increased towards the end of the test, in the case of the tellurium-lead. The results of tensile tests on the same materials, and carried out on the same machine at a "rapid" rate of straining, are given in Table VIII.

The foregoing experiments show that in the case of slowly applied strain the tellurium-lead gives an ultimate stress actually 50% greater than that of ordinary lead.

FIG. 1

Lead + 0·06% Te. Cold-rolled structure. × 10

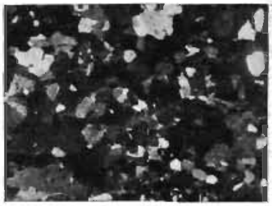


FIG. 2

Complete recrystallization in cold-rolled lead sheet. × 10

FIG. 3

Deformed grains in cold-rolled sheet lead + 0·06% Te. × 50

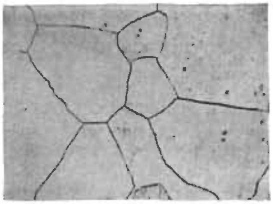


FIG. 4

Undistorted grains in cold-rolled lead sheet. × 50

FIG. 5

Incipient recrystallization in cold-rolled sheet ead + 0·06% Te. × 50

FIG. 6

Structure of cold-rolled sheet lead + 0·06% Te after 6 months. × 150

PLATE I

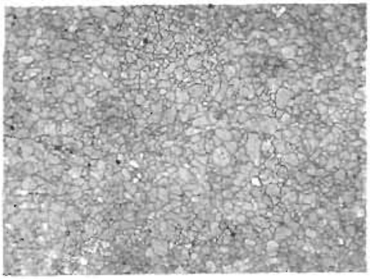


Fig. 7

Extruded section. Refined grain. Lead + 0·06% Te. × 50

Fig. 8

Lead extruded section. × 50

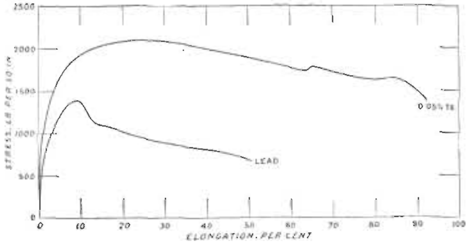


Fig. 11

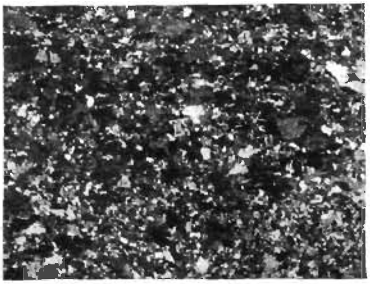


Fig. 9

Rolled sheet lead + 0·06% Te. Annealed for 1 hr. at 250° C.
× 10

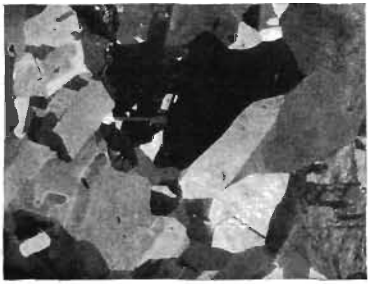


Fig. 10

Rolled sheet lead Annealed for 2 hr. at 150° C
× 10

PLATE II

The types of elongation and fracture of the tellurium–lead are the same in both the slower rates of applied stress. It is known that a metal will withstand uniformly distributed elongation in the tensile test to an excessive extent provided that: (1) it begins to yield well below its ultimate stress; (2) it is capable of work-hardening in a progressive manner when strained.

TABLE VIII

Tensile tests. "Rapid" rate of straining

Material	Ultimate stress, lb./in.^{2}	Elongation, % on 8 in.
Lead + 0·05% tellurium	2850	56
Lead	2350	53

These results are of significance when considering the practical applications of lead, particularly in the form of pipe. In such cases pliability is essential, together with the capacity to yield to the stresses met with in service; for example, by the freezing of contained water. This ability to yield should be combined with toughness if the local weakening which leads to early fracture is to be avoided.

Effect of frost.—It is clear from the foregoing tensile tests that tellurium–lead when strained behaves in a manner previously unknown in lead and lead alloys. The ability of tellurium–lead to work-harden when strained is a property of considerable practical value, and indicates that pipes will, in practice, withstand a much greater expansion before commencing to weaken locally. Freezing experiments illustrate the practical value of the work-hardening properties of the metal. Pipes of ordinary and tellurium–lead with internal diameter of ¾ in. and a wall thickness of 0·125 in. were taken from the normal works production. The pipes were filled with water and together were repeatedly frozen until bursting occurred. Suitable end plugs were designed for the pipes. The results of these tests are as follow:

Material	Number of freezings to burst Sample (a)	(b)	(c)
Lead	2	2	2
Lead + 0·05% tellurium	5	5	5

The pipes made from ordinary lead showed marked local distension after the first freezing, and fractured during the next freezing with the formation of a large bulge. The pipes of tellurium–lead were quite symmetrical after three freezings. After the fourth freezing a slight, but well-distributed, distension was noticed. At the fifth freezing failure occurred with a moderate local bulge. It has been observed that the number of freezings that a lead pipe will withstand is, to some extent, dependent on the length of pipe tested and the time occupied in freezing. For that reason the number of freezings quoted above should be taken as only comparative figures for lead and tellurium–lead tested at the same time and in the same conditions. Rapid hydraulic bursting tests, carried out on lead and tellurium–lead pipes of the same dimensions as those used in the freezing tests, gave the following results:

Material	Hydraulic bursting, lb./in.^{2}
Lead	725
Lead + 0·05% tellurium	800

Another sample of the same batch of tellurium–lead pipe was subjected to three freezings. When hydraulically tested after 24 hr., the pipe resisted an hydraulic pressure of 750 lb./in.^{2} before bursting. Even after three freezings, with the consequent reduction in wall thickness due to expansion, the resistance of the tellurium–lead pipe to hydraulic bursting was still maintained. In similar conditions a lead pipe burst after two freezings. This experiment reveals what may be described as latent strength—a property not indicated by the results of ordinary tests where strain is rapidly applied. In the application of lead and lead alloys where severe deformation is normally to be expected, initial softness and pliability, combined with an ability to develop toughness, are desirable. The "strength" of tellurium lead does not appear as hardness, but is more in the nature of toughness.

Fatigue tests.—It is well known that the fatigue resistance of lead can be increased by alloying with other metals,* but hitherto this method has involved a sacrifice in the characteristic properties of lead. For many practical applications advantage cannot be taken of the high fatigue-resistance of various lead alloys because of their inherent hardness and lack of ductility. The effect of tellurium on lead is such that the hardness is only slightly increased. By the kindness of Prof. B. P. Haigh, the fatigue-resistance of extruded lead containing 0·05% tellurium was determined in a Haigh fatigue-testing machine. On a basis of the range of stress which would not cause fracture after 10×10^6 reversals, the fatigue range was found to be $\pm 0{\cdot}50$ ton/in.^{2}, nearly three times that of ordinary lead.

General.—The manufacture of tellurium–lead presents no difficulties whatever, either in the preparation of the metal or in the processes of cold-rolling and extrusion. Owing to the extremely refined grain, the appearance of the extruded products is markedly superior to that of ordinary lead.

THE ADDITION OF TELLURIUM TO LEAD ALLOYS

Further investigation has shown that the effects produced by the addition of tellurium to lead are to some extent also produced by tellurium when added to the binary lead–tin, lead–antimony alloys, and to the ternary alloys lead–antimony–cadmium and lead–tin–cadmium. The addition of tellurium to lead–antimony alloys, in addition to improving their physical properties, increases their resistance to corrosion, particularly by chromium-plating solutions. The addition of tellurium to the above-mentioned ternary alloys produces a marked improvement in their physical properties, imparting to them some of the toughness characteristic of tellurium–lead; thus, in the course of the author's experiments, ternary alloys containing tellurium have been found to have double the resistance to frost of the ordinary ternary alloys.

The authors desire to express their thanks to the directors of Goodlass Wall & Lead Industries, Ltd. for permission to publish this paper; to Mr. C. A. Klein for much helpful criticism, and to Messrs. C. F. Ross, A. Lloyd, W. Hulme, and F. Hargreaves of the Research Laboratories for their help in the experimental work described.

* Beckinsale and Waterhouse, J. Inst. Metals, 1928, 39, 375. Townsend, Proc. Amer. Soc. Test. Mat., 1930, 30 (11), 395.

BAKER PERKINS, LTD.

When recently we paid a visit to Peterborough there seemed on approach to be two conspicuous landmarks. To the right of the station lay the spires of the cathedral, whilst on the left a rectangular building jutted into the sky. Possibly to call this building a "skyscraper" would bring forth the contempt of New York, but certainly the new offices of Baker Perkins merit the description as far as provincial England is concerned. The Westwood works of the company at Peterborough are still being expanded, and this building is one of the more recent additions.

NEW OFFICES BUILDING AT PETERBOROUGH TO ACCOMMODATE THE JOINT STAFFS OF WILLESDEN AND PETERBOROUGH CONSEQUENT UPON CENTRALIZATION OF THE BUSINESS.

There is perhaps little need here to speak in detail of the company's productions, for the Baker Perkins machines are well known to the baker, the launderer, and chemist, and are used in a host of other related industries. A few details of the Westwood works are however not without interest. We confess to being somewhat amazed at the size and scope of the works, for that original view of the "skyscraper" was a fair indication of what was to follow. Passing through the offices at the entrance we found ourselves immediately in the "machine shop" which covers an acre or two, and was in such a whirl of activity that the much-abused description "a hive of industry" seemed at last to be merited, for there were hundreds of lathes and other machines turning, finishing, polishing, and drilling the parts of numerous machines.

Close by was the "plate shop," dealing at one end with heavy steel plating, and at the other with lighter tinned material, and then there was the "assembling shop," where the machines take shape from their separate parts. One interesting machine here was capable of taking tablets of soap at one end, placing them in cartons, folding and gumming the ends of these, and turning them out at the other end ready for despatch at the rate of 130 a minute. In the shop dealing with constructional work an interesting job was the preparation of the steam tubes for baking ovens. These steel tubes are about an inch in diameter, and after being partly filled with water are sealed off at both ends. When they are heated in the ovens the water is converted into steam, and the temperature of the ovens is maintained at a constant level for a considerable time. To seal these tubes off efficiently and bend them to desired shapes is an operation of skill that is acquired only by long experience. Perhaps still more of an art is that of the moulders working in the extensive foundry, for many of the machines of Baker Perkins are built up on castings, ranging from massive bed-plates down to small parts that can be held in the hand, and nearly all of them are of complicated design. The wooden moulds for these castings are prepared in the "pattern shop" near by; an interesting feature here was the system by which the dusty air is drawn off and fresh air introduced into the building by large ventilator shafts.

From the chemist's point of view one of the company's most interesting productions is the well-known "Universal" mixing machine, in which two blades revolve at different speeds inside two semi-cylinders, intersecting in each revolution every part successively on the trough surface. For dealing with coarse materials the edges of the blades may be serrated to give a tooth-like action, whilst for mixing abrasive materials the blades are fitted with replaceable shoes, and the troughs have replaceable liners. The "Peerless" mixer, which is used in many food-processing factories, is also made at the Westwood works, and we were able to see the machine in every stage of assembly, from the rough main casting to the immaculate green-enamelled machine ticking over on test prior to despatch. We could mention many other machines being manufactured here, from air separators to soap machinery, for if variety is the spice of life Baker Perkins, Ltd. seem to have found it also to be the spice of successful business.

THE ASSEMBLING SHOP

The works show evidence of very careful planning, the departments for successive operations being grouped together in ordered sequence that makes for economy or production. We cannot remember having seen glass roofing used to a better advantage; this was only one indication of the consideration that is given to the working conditions of the 1700 employees in the Westwood works.

SOCIETY OF CHEMICAL INDUSTRY

OFFICIAL NOTICE

Annual Reports. The new volume of the Society's Annual Reports on the Progress of Applied Chemistry, 1932, Vol. XVII, is now ready. Copies may be obtained by postal application to the General Secretary, 46, Finsbury Square, London, E.C.2, and must be prepaid: Members 7s. 6d., non-members 12s. 6d.

BRISTOL SECTION

The annual general meeting of the Bristol Section was held on March 1 at the University of Bristol, Mr. R. D. Littlefield in the chair. A silver salver, note case and contents were presented to the hon. secretary, Mr. Arthur Marsden, who had occupied the position for more than 12 years and devoted much energy and time to the advancement of the section. Tributes to his energy and tact were paid by Mr. W. M. Jones and Prof. M. W. Travers, F.R.S.

Mr. Littlefield was re-elected chairman; Prof. F. E. Francis was re-elected vice-chairman; Mr. Jones as hon. treasurer and Mr. Marsdon as hon. secretary. Messrs. A. Sanders, T. Penny, R. Robertson, F. W. Rixon, and F. Adcock were elected to the committee and Messrs. W. O'Brien and J. Edwards were appointed as auditors.

At the close of the formal meeting Mr. Littlefield gave an address on "The Laboratory and the Board Room."

MONTREAL SECTION

About seventy-five members attended the meeting of the Montreal Section of the Society on January 25 in the Chemistry Building of McGill University, when Dr. William H. Barnes, lecturer in chemistry of McGill University, delivered a very interesting address on "Atomic Structure." In the first part of this paper Dr. Barnes dealt with the subject from the point of view of its historical interest, outlining the various atomic theories which had been formulated and the events in chemical history which had led to their development. Coming then to the subject of the modern conception of the structure of atoms, Dr. Barnes said:

In 1904, J. J. Thomson suggested that the atom might consist of a sphere of positive electricity containing concentric rings of electrons. Certain maximum numbers of electrons in any one ring were shown to represent stable arrangements and the total number of electrons was equal to the positive charge on the atomic sphere. The work of Rutherford, Geiger, Marsden, and others, on the scattering of α-particles by matter showed that these positively charged helium ions could penetrate very deeply into an atom. The positive charge cannot therefore be distributed on a sphere of atomic dimensions and the α-particle must be very small.

In 1911 Rutherford proposed the nuclear theory of the atom which is the foundation for all subsequent atomic models. He showed that an atom must consist of a small massive positively charged nucleus surrounded by electrons equal in number to the charge on the nucleus. In the same year van den Broek suggested that the charge on the nucleus is equal to the atomic number. This agreed with experiments of Rutherford and Nuttall which demonstrated that the nuclear charges of hydrogen and of helium are 1 and 2 respectively, and has since been confirmed by Chadwick for some of the heavier atoms.

On the basis of Rutherford's theory the hydrogen atom (mass 1, atomic number 1) must consist of a nucleus carrying one positive charge, together with one external electron. The atom of helium (mass 4, atomic number 2) has a nucleus with a positive charge of 2, so there must be two external electrons. The nucleus must consist of four positive charges (protons) and two electrons in order that the mass shall be 4 and the charge only 2. The α-particle therefore is identical with the helium nucleus. Lithium (atomic number 3) has an atomic weight of 6·940 which is an average of two isotopes of masses 7 and 6 respectively. The *Li* (7) isotope has a nucleus of seven positive and four negative charges, while in the nucleus of Li (6) there are six positive and three negative charges. In both cases the positive charge on the nucleus as a whole and hence the number of external electrons is equal to three.

The mechanism of radio-active disintegration receives a satisfactory explanation in terms of the Rutherford atom. It can be illustrated by the following incomplete sequence.

U_1 (mass 238, atomic number 92) has 238 positive charges and 146 negative charges in the nucleus and 92 external electrons. It loses an α-particle (4 positive and 2 negative charges) from the nucleus, thus becoming an atom of Ux_1 with a nucleus of 234 positive charges and 144 negative charges, and 90 external electrons. It therefore has a mass of four units less than U_1 and an atomic number of 2 units less. The loss of a β-particle (negligible mass, 1 negative charge) from the nucleus of Ux_1 results in the formation of an atom of Ux_2 with a nucleus of 234 positive and 143 negative charges, and 91 external electrons. Ux_2 therefore has the same mass as Ux_1 but is situated one place to the right in the Periodic Table.

It may be mentioned at this point that it is not yet clear whether the gamma-rays which accompany certain radio-active transformations have their origin in a movement of the nucleus as a whole or of its constituent parts.

In the original atom of Rutherford the external electrons move in circles about the nucleus so that the electrostatic attraction of the nucleus is balanced by the centrifugal force due to the rotation. On the basis of classical electrodynamics however a moving charge of this kind should radiate energy continuously and consequently the electrons should travel in continuously decreasing orbits until they fall into the nucleus. Planck in 1900 had however proposed a new theory of radiation (the Quantum Theory) which was extended by Einstein five years later. This theory assumes that the emission

and absorption of energy does not take place continuously but in bundles, packets, or quanta, which are proportional to the frequency of the oscillator involved.

Rutherford's model of the atom was stabilized by Bohr's invocation of the Quantum Theory in 1913. Bohr assumed that the electrons could move in certain circular orbits without radiating energy, the relative arrangement of the orbits being such that the movement of an electron from one orbit to another is accompanied by the absorption or emission of an integral number of quanta, or units of energy. This original extension of the Rutherford atom only accounts, however, for the principal features of the spectra of the simplest elements. Three years later Sommerfeld showed that much better agreement between observed data on optical and X-ray spectra and the atomic model could be obtained by adding certain elliptical orbits to the circular ones of Bohr. This also involved the consideration of the effect of the varying velocity of the electron travelling in an ellipse with the nucleus at one focus on the mass of the electron, and also the fact that the ellipse may precess about the nucleus. These improvements, although accounting satisfactorily for the main facts of spectroscopy, were inadequate for many of the finer details.

In 1923 de Broglie showed that a further improvement can be effected by the assumption that an electron in motion is accompanied by a wave of a certain frequency. The great success which has attended the use of the quantum theory indicates that it is often necessary to consider the energy of a train of electromagnetic waves as concentrated in discrete quanta. Therefore, however difficult it may be to picture the phenomenon, it is not unreasonable to consider that a material particle may behave as the energy centre of a train of waves.

Shrödinger in 1926 suggested that the failure of ordinary mechanics to account for the behaviour of atomic systems might be due to the habit of thinking about paths of electrons and nuclei instead of considering wave-fronts associated with such paths. On this basis he has built up his system of Wave Mechanics which has been able to handle phenomena such as the diffraction of electrons by crystals, which are inexplicable by the older classical ideas.

In 1925, shortly before Shrödinger's first paper on Wave Mechanics, the problem of atomic mechanics was approached in a different way by Heissenberg. His Matrix (or Quantum) Mechanics abandons any idea of describing the atom in terms of time and space or of setting up atomic models. It furnishes rules for calculating observable quantities characteristic of the atom in terms of directly measurable data. The attitude is reminiscent of Ostwald's advocacy of thermodynamics instead of kinetic theory considerations at the beginning of the present century. Shrödinger, however, has shown that Matrix Mechanics follows as a necessary consequence from his Wave Mechanics.

These developments have shown that the constituents of atoms are not quite the clearly-defined entities which appeared to be the case ten years ago. A slight digression is necessary at this point to trace briefly the parallel development of another type of atomic model in which the electrons do not move in orbits as in the foregoing dynamic type, but are at rest or else oscillate about fixed positions. This latter (or static) model developed out of the attempt to explain the facts of chemical combination more clearly than was deemed possible on the basis of a dynamic atom. It grew out of the suggestions of Abegg in 1904 that groups of eight electrons must be particularly stable to account for the relationship between valence and position in the Periodic Table. It received support from J. J. Thomson's model of the same year which showed that only a certain number of electrons could be added to any one ring and form a stable arrangement.

In 1916 Lewis and Kossel independently applied these ideas to the nuclear atom and reached somewhat similar conclusions. Commencing with the assumption of very stable configurations for the rare gases the chemical properties of the other elements may be attributed to a tendency to give up or take up sufficient electrons to attain an external configuration resembling that of the nearest rare gas in the Periodic Table. In Kossel's model the electrons are arranged in concentric rings rotating about the nucleus at the centre. Lewis suggested a static or fixed configuration of electrons which can best be described in the following way. Hydrogen has a nucleus carrying 1 positive charge and 1 external electron. Helium has a nucleus with a positive charge of 2 and two symmetrically placed external electrons. Lithium, with a positive charge of 3 on the nucleus, has two external electrons resembling those of helium in position and one further removed from the nucleus at the corner of an imaginary cube with the nucleus and two inner (helium) electrons at the centre. From beryllium to neon the nuclear charge increases from 4 to 10 and the external electrons fill up the unoccupied corners of the cube. Neon therefore has eight external electrons at the corners of a cube, two electrons inside the cube, and a nucleus of 10 positive at the centre. At sodium another cube is started outside the one which is complete at neon and this second cube (or third shell) is itself completed at the next rare gas argon.

The formation of ions is pictured as a transfer of electrons from the outer shell of one atom to the outer shell of another. If a lithium atom loses its outer electron it becomes a positively charged lithium ion with two electrons outside the nucleus, thus resembling the neutral helium atom. If a fluorine atom gains an electron it completes its outer cube of eight electrons, becoming a fluorine ion with a negative charge of one and an external structure like that of neon. The formation of non-polar compounds, such as F_2, is supposed to be due to a sharing of one or more pairs of electrons between the atoms concerned. For example the 14 external electrons of two atoms of fluorine can be arranged to completely fill the corners of two cubes, if two adjacent corners (one pair of electrons) are common to both cubes.

At about the same time J. J. Thomson brought his earlier views into conformity with the nuclear model but adhered to the static arrangement of external electrons by postulating a law of force between electrons and nucleus which would hold the electrons in fixed positions. This obviated the necessity for using the

Quantum Theory and suppressing the radiation from an electron moving in a Bohr orbit.

In 1919 Langmuir extended the Thomson-Lewis scheme in an attempt to derive satisfactory structures of all the elements, on the assumption that the electrons tend to form layers around the nucleus containing 2, 8, 8, 18, 18, and 32 electrons respectively. This was modified by Bury in 1921 who concluded that in order to account for the facts of valence the number of electrons in the outer shell must never exceed eight but under certain conditions intermediate layers can contain more than eight electrons.

The static atom lends itself more readily to the description of chemical phenomena than does the dynamic type. It is incapable however of accounting for the facts of spectroscopy. On the other hand, attempts to explain chemical properties in terms of the dynamic atom have been made with increasing success by Bohr, Sidgwick (1923), and Main Smith (1924).

On the basis of Wave Mechanics complete configurations for all the atoms have been worked out which not only account satisfactorily for spectroscopic data but are in harmony with the generalizations of the Periodic Table. It is not feasible, and only doubtfully possible, to express these structures in terms of time and space as these words are usually employed. In a general way it can be said that the electrons outside the nucleus each possess a single charge of negative electricity and behave as though they were the energy centres of trains of waves. They move in certain circular and elliptical orbits around the nucleus and the possible orbits are limited by definite energy considerations. The mass of the electrons varies with their velocity, they are spinning like tops, and their orbits may precess about the nucleus and will orientate themselves in definite directions when subjected to the influence of an electric or magnetic field.

The nucleus of an atom also has a very complicated structure of which present knowledge is still in an elementary state. Helium nuclei and electrons are projected out of radio-active atoms. Protons can be ejected under certain conditions when α-particles collide with the nuclei of other atoms. For example, if an aluminium nucleus of mass 27 is struck by an α-particle (mass 4) which it retains, a proton (mass 1) is ejected and a silicon nucleus of mass 30 is the result. Last year Chadwick showed that beryllium or boron atoms when bombarded by α-particles emit neutrons which are capable of ejecting protons from matter containing hydrogen and also from many, and possibly all, elements. The neutron has zero charge and a mass practically equal to that of the proton and is considered to be a close combination of an electron and a proton—possibly a proton imbedded in an electron.

It is probable that the structure of the nucleus is as complicated as the outer structure of the atom. It undoubtedly possesses a spin and there is evidence that its constituents (electrons, protons, helium nuclei, and neutrons) are in an orderly dynamic state and not merely packed together haphazardly. With the very satisfactory manner in which the external electrons can now be described on the basis of the new mechanics it is probable that increasingly rapid progress will be made in the highly complex realm of nuclear structure.

NOTTINGHAM SECTION

At a meeting on February 16, a series of short talks was given on some industrial problems.

Mr. S. Spray described some experiments on the corrosion of cast iron in which the graphitic carbon was present in coarse and fine forms respectively. He immersed each iron sample in dilute sulphuric acid together with a carbon rod, to which it was connected by a wire. This wire was removed at intervals, and electric measuring instruments inserted instead. Specimens with coarse graphite gave lower readings than those with fine graphite, but the loss in weight of the coarse specimens was greater than the fine. This result was not what he expected, as he had argued that higher reading should go with a greater loss in weight.

Mr. G. P. Storer mentioned a test for the estimation of bitumen in tar mixtures which consisted in adding dimethyl sulphate to the fractions of distillate, and reading the separated oil. This was considered to give reasonable results until an occasion when a negative test was obtained with a tar which the suppliers were certain contained the proper amount of bitumen. The conclusion was then reached that the test showed only petroleum products and was of no use for bitumen. He would like to hear of a satisfactory test for bitumen.

Mr. T. F. Heyes described a case of bad damage in processing of some socks of cotton backing plated with artificial silk. Fortunately some of the untreated socks were available, and the fault was tracked down to the artificial silk, which although responding fairly well to the usual physical tests, was shown by its copper number and fluidity of the 2% solution to be badly degraded. The yarn was a viscose artificial silk which had been dulled in process of manufacture, probably by the addition to the spinning solution of a liquid insoluble in viscose, and he suggested that the damage might have been connected with the dulling process.

Mr. G. E. L. Carter gave an account of some of the difficulties of the tanner due to the lack of uniformity between parcels of skins, skins in the same parcel, and between different parts of the same skin. The skins are graded during the various processes for differences in thickness and quality, for structural defects, and defects of the surface. The subtlest variations are found in texture; this is dependent on the health and well-being of the animal and the quality of its food, and also varies in different parts of the body. A section of skin from the butt has a pattern suggesting a tightly woven material: the bundles of fibres are woven in a fairly even pattern, those in the plane of the section often appearing at an angle of about 40° to the horizontal. The cross sections of bundles approximate to circles and there are few open spaces. In skin from the belly, on the other hand, the general effect is that of a loosely woven mat; the fibre bundles in the plane of the section are nearly horizontal, the form of the cross sections never approaches a circle and there are many open spaces. After treatment with lime sulphur, the hair is scraped off and the pulped fat gland and other tissue removed by squeezing. The duration of the lime sulphur treatment is important, some skins requiring longer than others. The internal structure of the skin becomes modified.

also during the process, and the structural character as it leaves the limes is retained throughout the remaining processes, so that any efforts to influence the skin towards uniformity of texture must achieve a more complete control of the modification of structure during the unhairing processes.

CHEMICAL SOCIETY

An ordinary scientific meeting was held on March 2, *Prof. J. F. Thorpe, C.B.E., F.R.S., Vice-President,* occupying the chair.

Dr. F. G. Mann discussed :

The Complex Metallic Salts of Sulphamide : an Optically Active Inorganic Salt.

Chelate co-ordinating groups may be divided into two classes : *(a) those which can fully saturate 6-co-ordination* metals, examples being ethylenediamine, the oxalate radicle, etc., (*b*) those which apparently never fully saturate such metals, since not more than two such groups can co-ordinate stably with one atom of the metal. Examples are dimethylglyoxime, which gives compounds such as $[Co(C_4H_7N_2O_2)_2(NH_3)_2]Cl$, and *αγ-diamino-β-hydroxypropane*, which gives

$$[(HO)_2Co\{(NH_2CH_2)_2CHOH\}_2]Cl.$$

It was earlier suggested (Mann, *J.*, 1927, 2907) that the configuration of such compounds was governed by a *steric factor*, which by *inducing a trans configuration* prevented co-ordination of the third chelate group.

Sulphamide, $H_2NSO_2NH_2$, has now been found to fall into this second class of chelate groups, since even when in excess it yields salts such as $Na[(H_2O)_2Rh(H_2N_2SO_2)_2]$ and $Na[(HO)(NH_3)Pt(H_2N_2SO_2)_2]$. The former, however, has been resolved into optically active forms, having $[M]^{5780}$ + 31 and − 34°, and has therefore the *cis* configuration. The formation of these *cis* compounds must therefore be determined by a *stability* factor, since under the conditions of the preparation an extremely unstable compound having three chelate groups has only a transient existence, and sheds its third group, giving the more stable *cis* di-chelate compound.

In certain cases the steric and the stability factors may act simultaneously, giving a mixture of the *trans and cis di-chelate compounds.*

The Chairman remarked that the paper was a notable contribution to the chemistry of optically active inorganic substances. He called attention to the fact that they had present with them that evening both the creator of the term "chelate" and the originator of the parachor.

Prof. G. T. Morgan said that Dr. Mann's communication was of special interest in that his use of the sulphamide radical as a chelate group in the production of *co-ordination compounds had in the case of the rhodium* salt led to the formation of a *cis*-derivative which was resolvable into optically active forms. There was on record only one other case of the resolution of a purely inorganic co-ordination compound, namely hexoldodecamminotetracobaltic chloride $[\{(NH_3)_4Co(OH)_2\}_3Co]Cl_6$, resolved into optically active forms by Werner in 1914.

Prof. C. S. Gibson observed that by analogy with bipentamethylene gold bromides, where the gold *atom is 4-covalent and co-ordinates with ethylene*diamine obviously in the *cis*-position, the groups now *attached to the gold atom having an octahedral configuration,* *cis*-co-ordination would be anticipated in Dr. Mann's compound.

Prof. J. Kenner discussed :

The Catalytic Decomposition of Nitroso-β-alkylamino ketones. Part I. A new method of preparing diazomethane, and evidence of the occurrence of diazotisation in the aliphatic series. [With E. C. S. Jones.]

Nitroso-β-alkylamino*iso*butylmethyl ketones have been prepared and shown to undergo catalytic decomposition by alkali. From the methylamino-compound diazomethane is thus produced, whilst the *n*-propyl homologue yields propylene and *n*- and *iso*-propyl alcohol. Unsaturated hydrocarbons and nitrogen also result from the decomposition of the nitroso-derivatives by mineral acids.

The Chairman remarked that Prof. Kenner had *described a great achievement in that he had been able* materially to increase the yield of diazo-hydrocarbons of the alphatic series. This would undoubtedly prove of considerable importance not only to scientific workers but also to industry.

Prof. G. T. Morgan remarked that it would be of considerable interest to treat the aliphatic diazohydroxide or diazonium hydroxide with a mineral acid at low temperatures in order to ascertain whether a purely aliphatic diazonium salt was capable of existence. Hitherto all diazotisable bases whether of the homocyclic division *(benzenoid, naphthalenoid, etc.) or of the* heterocyclic division (such as amino-pyrazoles, *-iso*oxazoles, or -thiazoles) contained the group $\geqslant C{\cdot}NH_2$. Diazotisation was performed on the salt such as $\geqslant C{\cdot}NH_3Cl$ when the three hydrogens were replaced by nitrogen to give $\geqslant C{\cdot}N{\cdot}Cl$. Hitherto it had been
‖
N
supposed that the unsaturated ring was essential to the *existence of a true diazonium salt.*

Prof. Kenner replied that experiments on the action of cuprous chloride and hydrochloric acid on nitrosoamines communicated to the Society some time ago arose from attempts to subject the nitroso-derivatives now described to the Sandmeyer reaction. The result, however, was the quantitative regeneration of the original amines.

Dr. R. P. Linstead discussed :

Investigations of the Olefinic Acids. Part VII. The Preparation of βγ Acids. [R. P. Linstead, E. G. Noble, and (in part) E. J. Boorman.] *Part VIII. Dissociation Constants.* [D. J. G. Ives, R. P. Linstead, and H. L. Riley.] *Part IX. The Addition of Hydrogen Bromide to Unsaturated Acids.* [E. J. Boorman, R. P. Linstead, and H. N. Rydon.] *Part X. The Formation of Lactones from αβ- and βγ-n-Butenoic and Pentenoic Acids.* [E. J. Boorman and R. P. Linstead.] *Part XI. The Formation of Lactones from some γδ-Acids and an Example of Ring–Chain (Lacto-Enoic) Tautomerism.* [R. P. Linstead and H. N. Rydon.]

This group of papers illustrates the capacity of an *ethylenic double bond to polarise at demand and* indicates the effect of neighbouring alkyl groups in

determining the direction of this polarisation and its result in additive reactions.

The polarisibility of the double bond is shown by measurements of the dissociation constants of a number of unsaturated acids. The dissociation is shown to be influenced by the alkyl substitution and by the proximity of the double bond to the carboxyl group. (Part VIII.)

These results are next correlated with those obtained from *a study of the addition of hydrogen bromide to the* same substances. (Part IX.) The direction of addition is *profoundly modified by the nature of the solvent. In* hydrocarbon solvents orientation is controlled by the carboxyl group and the bromine atom adds to the more distant carbon atom irrespective of the alkyl substitution. In the absence of solvent or in ether, the orientation of addition is determined by the alkyl substitution about the double bond and follows the Markownikoff rule. The addition to pure unsaturated esters proceeds in the same direction as that to the corresponding acids in hydrocarbon solvents. Remarkable inversions of the direction of addition are therefore found in acids containing *a terminal methylene group; for example.* vinylacetic acid yields γ-bromobutyric acid in toluene *but β-bromobutyric acid in ether or in the absence of* solvent: while its ester gives the γ-bromo-ester in the absence of solvent.

These results are further correlated with the capacity for self-addition (lactonisation) of unsaturated acids (Parts X, XI). Thus an acid $R^1R^2C\!:\!CH\cdot(CH_2)_x\cdot COOH$ may under suitable conditions yield a lactone $R^1R^2C\cdot CH_2\cdot(CH_2)_x$ or its isomeride $R^1R^2CH\cdot CH\cdot(CH_2)_x$

O———CO   O—CO

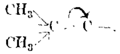
It is shown that. providing stereochemical requirements are satisfied, self-addition always occurs in the same direction as that of hydrogen bromide to the acid alone. *i.e.. so that the hydrogen atom adds to the same carbon* atom in each case. If this is not possible, tautomeric change but no lactonisation occurs (vinylacetic acid). γδ-*iso*-Heptenoic acid is reversibly converted into the corresponding δ-lactone at its boiling point, an equilibrium containing some 60% of lactone being formed.

This provides an exceptionally clear case of ring–chain tautomerism (Part XI).

Part VII is concerned with an examination of preparative methods.

The new results are considered in relation to the earlier work of Fittig, Fichter, and others, and to current electro-chemical theories of organic reactions.

The Chairman said that this was the most notable contribution to the chemistry of the unsaturated acids since Fittig published his classical researches 25—30 years ago. One of the most important results achieved by the author and his collaborators was the discovery of the existence of ring–chain tautomerism between an unsaturated acid and its lactone isomeride.

Dr. G. N. Burkhardt said that the authors' results give systematic data on the interaction between two groups, separated by moderate distances, in an aliphatic compound. Most previous systematic studies of, *e.g.*, the influence of groups on the properties of ·C:C· have been made more difficult to interpret by the nearness *of the substituent to the unsaturated system.* Formally the results for dissociation constants suggest that the double bond is enabling the electron repulsive effect of terminal Me to be transmitted past 2 or 3 single bonds to the carboxyl group. Dr. Linstead writes the initiation of this effect as:  Does this formulation imply a permanent change in the valencies in the double bond of the same type as is postulated in the course of the oriented addition of HBr, or is it an electrostatic or electron displacement effect? The ethylene bond will affect the stereochemical relations of the methyl and carboxyl groups as well as the possibility *of transmission via the double bond itself.*

Prof. R. Robinson communicated the following:

Dr. Urushibara, working in collaboration with Prof. Barger and myself, has observed that the direction of addition of hydrogen bromide to undecenoic acid in *toluene solution is influenced by the presence or absence* of traces of water. When perfectly dry materials are *used the product contains much 10-bromo-undecoic* acid but in the presence of a trace of water practically pure 11-bromo-undecoic acid is obtained (Walker and Lumsden). With more water 10-bromo-undecoic is again produced. It is extremely difficult to find a satisfactory explanation of these phenomena.

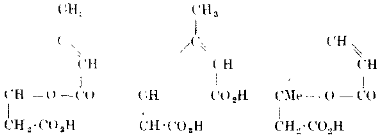
Prof. C. K. Ingold said that his original theory of solvent action in orientation (Solvay Reports, 1931, pp. 493—494) had recently been reproduced in too narrow a form. He had made it a distinguishing criterion of the direct effect (Ingold and Vass, J., 1928, 417) that because that effect traverses the medium it must be dependent on the transparency of the medium to local electric fields. In illustration he had *quoted* the addition of HBr to allyl bromide which exhibits solvent-dependence *essentially similar to that of the unsaturated acids now* considered: in transparent solvents orientation is controlled by the Br-atom (external, or direct. effect; "distant orientation"), and in opaque solvents by the atoms adjoining the unsaturated carbon atoms (internal, or inductive, effect; "local orientation"). The long-range character of the direct effect and the very local nature of the inductive effect are well established (Gane and Ingold, J., 1928, 1594; 1929, 1691; 1931, 2153). The original statement (Solvay Reports) referred to the various electrical constants which describe the action of a medium on a local field, and these constants, according to customary physical classification, form a series dependent *on poles, dipoles, quadrupoles, etc. In the form in* which the theory has recently reappeared, consideration is limited to poles, *and the extensive and accurate work* now described contains illuminating illustrations of the inadequacy of so imperfect a version. Thus, the acids, considered as solvents, exhibit "local orientation" and are therefore to be considered opaque, whilst the esters show "distant orientation" and accordingly are transparent. In the speaker's theory the former effect would be ascribed, not to ion-screening, but to dipole-screening in associated agglomerates containing closed circuits of dipoles and stabilised by the co-ordinative tendency of hydrogen. In connexion with the transparency of the esters in HBr-addition their structural capacity for

... ar formation was to be borne in mind. *Finally the* authors proved that the rules controlling the solvent dependence of HBr addition also apply to lactonisation as a clear evidence that the opacity of the acids is not due to the development of ions. As was indicated originally (Sol. ... Reports) a comprehensive programme of research on solvent effects in orientation is in progress at University College, London.

Prof. J. R. Partington and Mr. H. W. Ashton briefly indicated some results of measurements, which they have completed, of the dissociation constants of some unsaturated dibasic acids, and their alkyl and halogen derivatives, as determined by electrometric titrations with the quinhydrone electrode. The acids investigated were maleic, fumaric, citraconic, mesaconic, monobromomaleic, monobromofumaric, monochloromaleic, and monochlorofumaric. Maleic and fumaric acids are distinguished by the fact that whereas the titration curve for fumaric acid is similar to that for a monobasic acid, the curve for maleic acid shows a marked inflexion *in the middle, due to the fact that in this case* K_1 is considerably greater than K_2. With alkyl substitution, whilst the resulting acids are weaker, the same difference *between the two types is maintained. Halogen substitu*tion renders the acids stronger. However, in the case of bromomaleic acid the inflexion in the curve is very *slight, whilst in the case of chloromaleic acid it is absent*, indicating that halogen substitution not only increases the acidity, but also reduces considerably the ratio K_1/K_2.

Mr. W. F. K. Wynne-Jones said that the authors assume that the tendency of an acid to lose a proton may be measured by the dissociation constant of the *acid in water. It has however, been shown by Gold*schmidt that the relative strengths of acids vary considerably from one solvent to another; thus in water *o*-nitrobenzoic acid has a dissociation constant roughly 4 times as great as that of 3 : 5-dinitrobenzoic acid, whereas in ethyl alcohol the constant of the latter acid is more than 3 times as great as that of the former. Such changes occur even with closely allied acids, and consequently the relative dissociation constants of acids in any particular solvent cannot be regarded as a measure of their tendencies to lose protons.

Dr. R. J. W. Le Fèvre remarked that the degradation of 3-nitro-*p*-cresol [to β-methyl-γ-crotonolactone-γ-acetic *acid (I)] described in 1914 by Pauly, Gilmour, and Will* could scarcely have proceeded through the intermediate (II), since this should, on Dr. Linstead's results, have *lactonised to give (III) rather than (I)*.



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Dr. Linstead replied that with regard to the addition *of hydrogen bromide, the authors had themselves been* attracted to the idea that the difference between the direction of addition to unsaturated acids containing the *vinyl group and that to their esters* was connected with the association of the former, but they had found it difficult to reconcile this with the known association of *organic acids in hydrocarbon solvents*, in which they added hydrogen bromide in the same direction as their esters.

It appeared probable that the effect of the double bond on the dissociation of an unsaturated acid was transmitted internally, as it diminished rapidly with recession from the carboxyl group.

With regard to the danger of drawing conclusions as to polar factors operating in acid molecules from their dissociation constants, the authors felt that the concordance of the results obtained by the physical and chemical methods justified the use of the former, providing it was applied on a comparative basis to a range of compounds showing small variations in structure.

Dr. Burkhardt afterwards communicated the following: One of the two cases quoted by Dr. Wynne-Jones involves a substituent *ortho* to the carboxyl group of *which the dissociation constant is being considered*. In such cases the interaction between the groups would be affected by different solvents according to laws quite *different from those concerning more remote groups*. The influence of *ortho* groups on dissociation constants is notoriously complex.

INSTITUTE OF CHEMISTRY

At the 55th annual general meeting of the Institute of Chemistry held in the Hall of the Institute in Russell Square, on Wednesday, March 1, the Meldola Medal was *presented* to Dr. Leslie Ernest Sutton, of Oxford, and the Sir Edward Frankland Medal and Prize to Mr. Leslie Young, of the Royal College of Science.

In *moving the adoption of the Report* of Council, the President, Dr. G. C. Clayton, C.B.E., M.P., remarked on the steady growth in membership, the sound financial *position, and the increasing activity of the Institute.*

The Institute had received suggestions in which might be detected a measure of kindly criticism of chemists and *technical men, especially such as aspire to positions of* responsibility in industrial undertakings. For positions of control, science alone did not suffice; the chemist, like anybody else, must acquire much knowledge and experience and become endowed with those not less important qualities of character, judgment, and tact, which responsibility entails.

Not only competition, but discovery and invention, together with modern methods in administration and management, had contributed to the existence of conditions which were bewildering to economists and financiers. These difficulties were not new; they were only presented in a more acute form than even when mechanization of industry first started. It was for chemists to put our old industries in the most favourable position to meet competition, and even more to branch out into new lines, especially new industries which, by giving employment, would absorb some of those displaced by world competition in many of the heavy industries.

Prof. J. F. Thorpe, C.B.E., F.R.S. was elected President in succession to Dr. Clayton, and the officers and members of Council for 1933—34 were elected as

...lows: *Vice-Presidents:* Messrs. W. J. A. Butterfield, C. Clayton, A. E. Dunstan, F. G. Edmed, G. G. Henderson W. H. Roberts. *Hon. Treasurer:* Mr. P. H. Kirkaldy *Members of Council:* Messrs. C. O. Bannister, ... Brady, J. C. A. Brierley, R. Bruce, R. M. Caven, ... M. Comber, H. E. Cox, C. H. Desch, C. Dorée, H. D. Elkington, G. D. Elsdon, A. E. Everest, A. G. Francis, ... F. Gordon, R. H. Greaves, W. R. Hardwick, I. M. Heilbron, The Rt. Hon. Francis Robert, Lord Henley, H. H. Hodgson, G. E. Holden, R. H. Hopkins, E. B. Hughes, J. R. Johnson, G. King, J. G. King, A. G. G. Leonard, J. H. Lester, W. J. S. Naunton, G. H. Perry, E. K. Rideal, W. Rintoul, E. Russell, S. Smiles, F. Southerden, W. Wardlaw, H. B. Watson, E. J. Way, J. Weir, A. W. M. Wintle.

CORRESPONDENCE

VISCOSITY OF COAL TARS AND PITCHES

SIR.—The article by Mr. H. Pickard on "The Measurement of the Viscosity of Coal Tars and Pitches" published by the South Metropolitan Gas Company in 1932, and the comments on it by Dr. E. F. Armstrong (cf. CHEM. & IND., Jan. 6, 1933, p. 4) are of interest to us and worthy of further comment. In Mr. Pickard's paper data are given which show the two asphalts he used to be what Dr. Armstrong calls "pseudo-viscous." In another paper (*Fuel in Science and Practice*, **10**, 352—369, 1931) E. V. Evans and H. Pickard state that the asphalt which they used belonged to the class of plastic materials. Neither conclusion is in agreement with the results which we have obtained on various types of asphalts containing either a small amount of or no mineral filler.

A short time ago we performed some experiments on asphalts using a method developed by E. C. Bingham and R. A. Stephens. They described their method before the Society of Rheology at the 91st meeting of the American Association for the Advancement of Science held in Atlantic City, New Jersey, December 27—31 1932. It is expected that this paper will be published in the near future. Bingham and Stephens measured the viscosity of rosin and coal-tar pitch at temperatures ranging from 20° to 60° C.

Through the courtesy of Prof. Bingham the method was described to us some time before the presentation of the paper mentioned above, and we adapted it to the investigation of the rheological properties of asphalts. Using materials of about 60 penetration (a load of 100 grams on the needle of the penetrometer for five seconds at 25° C) we found that between the temperatures of 15° and 35° C steam refined asphalts from Venezuelan and Mexican crude petroleums as well as fluxed Trinidad Epuré and fluxed Bermudez Lake Asphalt were all viscous liquids. Air blown asphalts however, did not fall into this class of materials since the apparent viscosity decreased with increase in shearing stress. Experiments at temperatures higher than 35°C are already under way.

In the light of our experience we feel that it is misleading to report data on the type of flow of an asphalt without giving information as to its source and method of production. In addition, such general characteristics as the penetration and softening point would also be of value.

We are, Sir etc.,
The Barber Asphalt Co.,
Technical Bureau, Research Division,
R. N. TRAXLER and C. U. PITTMAN

New Jersey, U.S.A.
Feb. 24, 1933

OUR MILK MUDDLE

SIR,—"The call is to chemists . . . to set to work to find out how our cattle should, can, and shall be fed." "H. E. A." in CHEMISTRY AND INDUSTRY, p. 157.

Agreed. Set up a Royal Commission *ad hoc*. But the Reorganization Commission for Milk, whose Report so disappoints "H. E. A.," was set up to "prepare a scheme for regulating the marketing of milk:" an urgent task if the bottom is not to fall out of the milk market. The scheme comes not a day too soon and any attempt to load it with machinery for improving the quality of milk would have delayed its appearance and jeopardized its chance of acceptance, unamended, by the industry. Moreover, as "H. E. A." himself points out, the Commissioners were not competent to undertake the task he wants to see undertaken.

Having justified the Reorganization Commission, who steered an amazingly safe course through seas unknown to them, I am with "H. E. A." that the time is ripe for setting up a Milk Commission comparable with the Rivers Commission of 1868. It should be hurried into existence and then hurried no more. There are years of work to be done. At the moment a very strong committee, presided over by Sir F. Gowland Hopkins, is inquiring into Disease among Milch Cattle. There is reason to believe they are being pressed to report quickly. For that there may be justification. But if, among their recommendations, they included the setting up of such a Commission as "H. E. A." demands, we might get it. Will "H. E. A." offer to give evidence before them and make clear to the whole Committee, what some individual members must know, that the appointment of a Milk Commission, with wide terms of reference, is long overdue?

I am, Sir, etc.,
G. C. JONES

London
March 3, 1933

THE STRUCTURE OF ASCORBIC ACID

SIR,—We have shown previously[1] that ascorbic acid (hexuronic acid) gives on oxidation oxalic acid and threonic acid. We have now completed our examination of the configuration of the latter acid and have proved it to be *l*-threonic acid, since on oxidation with nitric acid it gives *d*-tartaric acid. Ascorbic acid is therefore related in stereochemical configuration to *l*-sorbose.

The same threonic acid is obtained by oxidizing with alkaline hypochlorite the highly characteristic product (A) produced from ascorbic acid by the action of aqueous iodine. These observations confirm the view that on reversible oxidation ascorbic acid is transformed into a

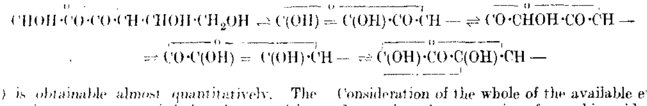
substance which can react as the structure (I) indicated in our former communication.

$$\text{(I)}\quad COOH\cdot CO\cdot CO\cdot CHOH\cdot CHOH\cdot CH_2OH \rightleftharpoons COOH\cdot CO\cdot C(OH) = CH\cdot CHOH\cdot CH_2OH\quad \text{(II)}$$

Further investigation has revealed that the mode of formation and the properties of (A) are complex. At *the moment of formation (A) does not exist as a free* acid, but titrates like a lactone. In this condition it does not show selective absorption, has a high positive rotation in water and gives a cryst. phenylhydrazine derivative (red, m.p. 216°). When the aqueous solution of (A) is kept the rotation slowly falls and a moderately intense absorption band makes its appearance at 295 mμ. When equilibrium has been reached ($[\alpha]_D$ 6°, approx.) a different phenylhydrazine derivative (yellow, *m.p. 210°) is obtainable almost quantitatively.* The mutarotation is not accompanied by decomposition since the final product can be reduced to ascorbic acid. *If the solution undergoing mutarotation is made alkaline* the band at 295 mμ is replaced by two very intense bands at 265 and 340 mμ, which on acidification move to 245 and 300 mμ. The substances involved are extremely labile and there is evidence to indicate that (A) in alkaline solution can undergo self-oxidation and reduction with partial regeneration of ascorbic acid (which has a band at 265 mμ in water, moving to 245 mμ in acid solutions).

The above phenylhydrazine derivatives have the same elementary composition and appear to be derived by the condensation of 2 mol. of phenylhydrazine with 1 mol. of a substance $C_6H_6O_6$. Ascorbic acid gives a cryst. di (phenylhydrazine) derivative (dark red, m.p. 187°) which is not identical with either of the other two and is derived from $C_6H_8O_6$. It is probable therefore that the oxidation of ascorbic acid by aqueous iodine consists in effect, of the removal of two hydrogen atoms, and the *reversible nature of the change suggests a specially* situated group of the type $>CHOH \rightleftharpoons >CO$. [Compare the views of Karrer,[2] who has given analytical evidence *in favour of the formula $C_6H_6O_6$ for (A).] The oxidation* product gives little furfural with HCl, in strong contrast with ascorbic acid and its methyl ethers.

Structure (I) which conceivably can lactonize and can react as a furanose and as a pyranose sugar and in a variety of enolic modifications remains the basis for interpreting the properties of ascorbic acid, the formula of which must be derived from one of the modifications of (I) by removal of an oxygen atom or by addition of two hydrogen atoms to the lactone. One method (Structure II) which accounted for the chemical and crystallographic data was put forward some time ago. Before suggesting (II) we had carefully considered structures of the furane and pyrane-carboxylic acid type (one of which has recently been advanced by Micheel and Kraft[3]) but we rejected them principally because they were incompatible with the crystallographic and *X*-ray *observations. These observations still hold and moreover* cyclic or open chain formulæ of this type are difficult to reconcile with the new facts. We consider therefore that attention *must now be given to the possibility that* ascorbic acid possesses a different type of structure related to (I), but depending for its acidic properties on an activated -OH group and not on a true -COOH group. *In studying ascorbic acid we have been impressed by* the analogy between its properties and those of glucosone and its derivatives (which show acidic properties) and we *would suggest the possibility that ascorbic acid may* in fact be 3-keto-*l*-sorbosone. This substance would be capable of reacting in many tautomeric forms (including both furanose and pyranose types) and the following scheme outlines the possibilities open to the furanose structure :



Consideration of the whole of the available evidence has shown that the properties of ascorbic acid can be adequately interpreted on the basis of the above structure *which, in addition, conforms with the stringent require*ments of the crystallographic and *X*-ray measurements.[4] Messrs. R. W. Herbert, E. G. V. Percival, R. J. W. Reynolds, and F. Smith are joint authors with me in this work.

I am, Sir, etc.,

E. L. Hirst

References

[1] Cox, Hirst and Reynolds, Nature, 1932, **130**, 888.

[2] Vierteljahrschrift d. Naturforschenden Ges. in Zürich, 1933, **78**, 9.

[3] Nature, 1933, **131**, 274. [4] Cox, Nature, Aug. 6, 1932.

Birmingham University
March 4, 1933

PERSONAL AND OTHER ITEMS

We regret to record the death on February 16 of Dr. George P. Adamson, director of research of the General Chemical Co. of America, in 1927, and a member of this Society since 1895. Dr. Adamson was born in Philadelphia in 1864. As a member of the firm of Baker & Adamson he was prominently associated with the progress of American chemical industry, whilst he took great interest in the welfare of several scientific societies, becoming a director of the American Chemical Society. Although he retired in 1927 he had remained particularly interested in research undertakings, and he will be missed, both as a friend and advisor, by many hundreds of chemists in America.

We deeply regret to record the death on March 2 of Dr. Henry Snape, O.B.E., one of the oldest members of the Society. Dr. Snape joined the Society in 1888, the year of his appointment to the position of professor of chemistry at University College, Aberystwyth, a position which he held until 1901. From 1901 to 1919 he was director of education in Lancashire, and took a leading part in educational activities in this country. He was chairman of the Association of Directors and Secretaries of Education, served on the Secondary School Examinations Council, and was associated with several other organizations. He held the D.Sc. degree of London University, the Ph.D. degree of Göttingen,

and had studied also at Berlin. In addition to contributing to a number of scientific journals, he prepared the third edition of Humpidge-Kolbe's "Inorganic Analysis."

The Society has lost a distinguished member by the death at his home at Northwich, Cheshire, on March 4, of Mr. G. W. Malcolm, M.B.E., M.I.Mech.E., M.I.E.E., at the age of 62. Mr. Malcolm served his engineering apprenticeship with Messrs. J. & H. Gwynne, and was later with the Pacific Steam Navigation Co., and the Naval Armament Construction Co., before taking up an engineering appointment in Mauritius in 1892. In 1908 he began an association with the Salt Union which lasted until the time of his death. As chief engineer of the Union he originated the process of supplying electric power as a by-product of salt manufacture, resulting in the formation of the Mersey Power Co. for supply to Widnes and Runcorn. He became managing director of both the Salt Union and the Mersey Power Co. and was actively concerned with a number of industrial companies. He was well known to chemical manufacturers as chairman of the Joint Industrial Council for the Chemical Trade, the Chemical Employers' Federation, and the Salt Compensation Board, whilst he was a member also of the Works Technical Committee of the Association of British Chemical Manufacturers.

Mr H. A S. Gothard. A.M.I.Chem.E. (managing director of Messrs. G.K.S. Combustion Co., Ltd., 11, St. Mary-at-Hill, London, E.C.3, Telephone:—Royal 3818), has completed an arrangement whereby he becomes sole distributor for the products of Messrs. Nichols Compressors, Ltd., Northallerton, Yorks, for London and the home counties.

Mr. James Herschel has retired from the position of secretary of the Bradford Dyers' Association on reaching the age limit, after 26 years' service. He is succeeded by Mr. C. J. Rose.

We regret to record the death in America of Mr. E. R. Smith, chief of the St. Louis Laboratory of the U.S. Food and Drug Administration, a position he had held since 1920. Mr. Smith had made special studies of food and drug adulteration with particular reference to legal requirements, and he was a valued member of several scientific societies in America.

Mr. W. W. Kay, M.Sc., at present assistant lecturer, has been appointed lecturer in chemical pathology in the University of Manchester.

Mr. C. M. Stuart, F.C.S., F.I.C., for thirty-four years headmaster of St. Dunstan's College, Catford, left estate of the gross value of £36,283, with net personalty £34,461.

London Section

Dr. J. J. Fox, O.B.E., Deputy Government Chemist at the Government Laboratory, Clement's Inn Passage, London, has been elected chairman of the London Section of the Society for the year 1933—34.

Chemical Society: Announcements

On March 2 Fellows were reminded that on March 16 Dr. G. F. Marrian will open a discussion on "The chemical constitution of œstrin," and that the fifteenth Faraday Lecture entitled "The relations between stereochemistry and physics" will be delivered by Prof. Dr. P. Debye in the lecture theatre of the Royal Institution, London, on Wednesday, March 29, at 5.30 p.m. Applications for tickets for the lecture should be addressed without delay to the assistant secretary.

On April 6 the ordinary scientific meeting will be devoted to the commemoration of Priestley's life and work: papers will be communicated by Prof. A. N. Meldrum, Sir Philip Hartog, and Sir Harold Hartley.

Food Group

The next meeting of the Food Group of the Society, which will be held at Burlington House on March 22, at 8 p.m., will take the form of a members' meeting at which a number of short papers will be contributed. (For titles of papers, see p. vi.)

An invitation to attend the Congress of the American Association of Cereal Chemists at Chicago on June 5, 1933, has been extended by the Association to any members of the Food Group who should be in the United States at that time.

The Royal Society

Candidates recommended for election into the Royal Society include the following: Prof. J. B. Collip, Professor of Biochemistry, McGill University, Montreal: Prof. H. M. Dawson, Professor of Physical Chemistry, Leeds University: Dr. H. J. Gough, Engineer, National Physical Laboratory, Teddington: Dr. Harold King, Chemist, National Institute for Medical Research, Hampstead; and Prof. J. E. Lennard-Jones, Plummer Professor of Inorganic Chemistry, Cambridge University.

Royal Visit to Chemical Works

The St. Helens Cable & Rubber Co., Ltd. was honoured recently by a visit paid by H.R.H. The Prince of Wales to its works at Slough. The Prince showed great interest in the manufacture of "Cabtyrit" linings for chemical plant, electric cables, rubber floorings, bakelite mouldings and others of the firm's productions, and as a memento of his visit autographed a cameo moulding of himself made some years ago in black and white rubber.

Vitamin Advisory Board in U.S.A.

A Vitamin Advisory Board, consisting of fonr members of the U.S. Pharmacopœia Board of Trustees, with, in addition, Mr. E. Fullerton Cook as chairman, has been established in America to help physicians and pharmacists to give patients vitamin preparations of standard potency. The Board will supply scientific workers with the new international vitamin standard preparations and will also distribute "reference cod-liver oils" of known vitamin-*A* and vitamin-*D* potency.

British Standards Institution

The latest B.S. Specification (No. 479—1933) issued by the British Standards Institution is concerned with the standardization of coal tar products and will be of especial interest to producers of coal tar naphthas. It will be a valuable asset also to those user sections of industry such as manufacturers of soap, rubber, varnishes, and dyes in which these products play an important part.

The advantages of being able to market the various fractions of tar distillates to a standard specification has

been realized by the principal producers for some time and the National Benzole Association set up a Committee which carried out an excellent piece of work in the preparation of specifications for the more general light oil products used in commerce. These are now issued as British Standards after review by a representative committee under the Chemical Division Council. The three grades of naphtha dealt with by the publication are coal tar solvent naphtha (sp. gr. 0·855) heavy coal tar naphtha (sp. gr. 0·860 to 0·910); and heavy coal tar naphtha (sp. gr. 0·855 to 0·915).

A complete specification is given for each grade and includes amongst other things, requirements for distillation range, specific gravity, freedom from impurities such as water, acids, alkalis, etc., and residue on evaporation. Detailed information as to the manner in which the various tests are to be made is given in the appendices and conforms to the recommended methods prepared by the Committee for the Standardization of Tar Products Tests.

Copies of this B.S. Specification (No. 479—1933) are obtainable from Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d., post free.

International Zinc Cartel

Conferences which have taken place at Brussels between the representatives of the zinc producers have culminated in an agreement to prolong until July 1 this year the existing understanding between the producers of Great Britain, Belgium, France, Italy, Poland, Australia, Canada, South Africa, and Mexico. By this agreement annual production remains fixed at 45,000 tons. Stocks existing at present amount to 148,000 t., and if, before July 1, stocks should increase to 155,000 t. factories which have exceeded their quotas will be restricted to output below their normal quotas. A meeting is to be held at a later date to settle the basis on which the cartel may be renewed for a further two years from July 1.

The Nomenclature of Chemistry

The American Pharmaceutical Association has for disposal a number of copies of the reproduction (from the original—1796) of "A New Nomenclature of Chemistry proposed by De Morveau, Lavoisier, Berthollet and Fourcroy, with Additions and Improvement by Lyman Spalding, M.B., Lecturer on Chemistry in Dartmouth University."

Dr. Lyman Spalding is the father of the United States Pharmacopœia, now in its 11th Decennial Revision. Copies of the book can be obtained from the American Pharmaceutical Association, 10W. Chase Street, Baltimore, Md., a charge of $1 per copy, post paid, being made.

International Union of Chemistry

The Third Report of the International Committee on Atomic Weights has recently been published and will in due course be noticed in these columns. The International Union is proposing to publish an International Table of thermo-chemical data and requests that authors who have published papers on thermochemistry within the last five years should send two copies of their papers to Dr. L. J. P. Keffler, The University, Liverpool.

REVIEWS

PERFUMES, COSMETICS, AND SOAPS: WITH ESPECIAL REFERENCE TO SYNTHETICS. By W. A. *Poucher.* being a Treatise on Practical Perfumery. Vol. II. 4th edition. Pp. xv. + 599. London: Chapman & Hall. 1932. 30s.

The fact that this very practical work is now in its fourth edition speaks for itself as to the value placed upon it by the practical perfumer. The present edition follows generally the plan of previous editions, with additions and modifications to keep it up to date. A novelty consists in a colour chart, the work of Mr. Dew Capey, A.R.C.A., to assist the practical man to colour his cosmetic preparations. In general it may be said that the work is eminently practical throughout, touching but lightly on the chemical side, such as the enumeration of constituents of various perfumes and flavours. It is, as it claims to be, "a treatise on practical perfumery," leaving the more chemical aspects to the purely theoretical works on the subject. A short historical sketch of the history of the perfume is given, but not stressed, only 17 pages being devoted to it. Another 30 pages or so are devoted to a short account of the researches of chemists on the formation of the perfume in the plant, with a very brief account of the methods by which they are obtained therefrom. The very fanciful classification of odours on a musical scale basis by Piesse, which has no foundation in scientific or other facts is reproduced at pp. 60—62, and might well have been omitted, as we think might the whole of the short chapter IV "Odour classification." Chapter V deals with fixation, one of the first bases of the perfumer's art, and is a chapter of considerable value. Pp. 91—243 are usefully employed by a series of monographs on flower perfumes, and for those who are not seeking formulæ to use in their business, is the most interesting part of the book. We now have a wide range of formulæ in all sections of perfumery, leaving each to choose or modify his own. The author is versatile and appears to have set out with the determination to leave no byeway unexplored. For example, there is a short chapter on tobacco, and if one wishes to find a formula for preparing snuff, it will be found here. A short chapter on fruit flavours is included in the first part of the book, and although it would not be unfair to say that practically no essence maker of any standing makes his essences on any *published* formula, those given in this chapter are the best we have seen published for a considerable time, and are nearer the actual working recipes in use to-day than the old rubbish which has been reproduced from book to book for generations.

Part II, commencing at p. 385, deals with cosmetics, and a mine of useful information is to be found here. There is an excellent chapter on skin creams and lotions, although, perhaps, all the chapters in this section are equally good. There is a useful appendix, whilst the book is well produced and may be said to be the best work that has appeared in the English language on the purely practical side of perfumery. It will no doubt go through many more editions.

Perhaps in the next edition the author and publishers might consider whether it might not be well to adhere to the usual convention adopted in technical books, and

omit the dozen pages of advertisements of perfume materials and plant, which are styled "Guide to the Purchase of Materials and Plant." E. J. P.

ANALYSIS OF FUEL, GAS, WATER, AND LUBRICANTS. By S. W. Parr. 4th edition. International Chemical Series. Pp. xv + 371. London: McGraw-Hill Publishing Co., 1932. 18s.

This book was originally designed about 21 years ago as an effort to introduce into an already overcrowded engineering curriculum some knowledge of analytical methods for University students of mechanical engineering. It has been widely used particularly in America, and the revision of the 4th edition was nearly completed when Prof. Parr died, the work being concluded by friends and former students. In an appreciation by Porter we are reminded of some of Prof. Parr's outstanding achievements, particularly with reference to the chemistry of coal and the calorimetry of fuels.

Part I, containing 22 chapters, consists of a synopsis of Dr. Parr's lectures on the origin, classification, and properties of solid, liquid, and gaseous fuels, together with their treatment and efficient use. Lubricants, and the characteristics and treatment of industrial and boiler waters are also dealt with. Dr. Parr has succeeded in producing, in the sections on power, the development of fuel research and calorimetry in America, a desire for further information which he proceeds to satisfy by his treatment of the constitution of coal and its classification, oxygen absorption, ignition temperature, storage, combustion, and fundamental properties in relation to carbonization, to mention only a few of the chapter titles. The second part of the book, containing 10 chapters, is devoted to details of laboratory and analytical methods for the sampling and analysis of fuels, gases, waters, and lubricants, the treatment being uniformly good. The appendix contains 15 useful tables and there are 101 illustrations together with a good index, while the printing and binding are excellent. It is a very readable book.

A. MARSDEN

DIZIONARIO PRATICO DEGLI ALIMENTI. By E. Santangelo. Pp. 1 + 408. Milano: U. Hoepli, 1932. Lr. 50.

In his introduction the author deals briefly with digestion, assimilation, and excretion, and outlines the problems of nutrition and the daily ration of man. He explains also the importance of food elements, proteins, carbohydrates, fats, vitamins, and water in metabolic processes. Though a condensed summary on these subjects, it is undoubtedly the best part of the book.

In the dictionary itself the principal items contain notes on origin, preparation, composition, and tests of purity of foodstuffs, as well as on their food value, digestibility, contamination, and adulteration. In 300 pages this ambitious scheme naturally could not be carried out with exhaustive thoroughness. The dictionary is meant to be a popular exposition concerned mainly with articles of diet, dishes, and delicacies preferred in Italy, but appeals also to everyone who is addicted to the consumption of quite uncommon foods, such as hippopotamus, ornithorhyncus, hystrix, fox, green lizard, white ants, fish milk, and hashish. The information on food not indigenous to Italy is not always correct; for example, under "mustard" it is reported that "English mustard is prepared with addition of wheat flour, salt, and cayenne pepper" and "Pudding is the *national dish of England*. . . . The variety most common in England and much used at Christmas is *Plumcake*"!

The third part of the book consists of a series of schemes of diet in tabular form for man at different stages of life and following different avocations, and special cases are considered, such as that of the vegetarian, and the person undergoing physical training. Each table contains a commentary explaining why certain foods are to be consumed or avoided for the purpose in view. Schemes of invalid diet are also given for diseases such as hæmophilia, cancer of the stomach, in the therapy of which the guidance of a popular book, however good, is perhaps inadequate. Nevertheless, Dr. Santangelò is to be congratulated on his attempt to popularise a subject of real and widespread interest.

EXTRA PHARMACOPŒIA OF MARTINDALE AND WESTCOTT. Revised by W. H. Martindale, Ph.D. 20th ed. In two volumes. Vol. I. Pp. xlvii + 1216. London: H. K. Lewis & Co., 1932. 27s. 6d.

Since 1928, the year in which the previous edition of this *vade mecum* was issued, not only have several new national pharmacopœias been published, but much information on non-official preparations, remedies, and methods of treatment has become available, hence the necessity for a complete revision of the book. First published in 1883, it supplied a long-felt want, and in the fiftieth year of its publication "Martindale" is more useful and more popular than ever before. It is a book to which anyone concerned with *materia medica* can turn with the utmost confidence and with the sure knowledge that it will either furnish the required information or indicate where the information is to be found. The text of this first volume has been almost entirely reset, and the appearance enhanced, whilst the inclusion of a synopsis of the principal additions and changes effected in the 1932 B.P. indicates the efforts which have been expended to bring the subject matter up to date.

COMPANY NEWS

BRADFORD DYERS' ASSOCIATION, LTD.

At the annual meeting of the Association (financial results, cf. CHEM. & IND., Feb. 24), Sir Thomas Robinson presided in the absence of the chairman, Mr. George Douglas, whose speech was read. In his report, Mr. Douglas said that total trade had increased compared with 1931, but was offset by lower prices. The payment for dyewares was £50,000 in excess of 1931 prices. The industry had had to suffer a 10% tariff in addition to the increase which was inevitable on imported dyestuffs following the departure from the gold standard. The board felt as strongly as ever on the action of dyestuffs manufacturers of Great Britain in advancing prices when in every other section of the industry wages were being lowered, and prices reduced. The American company had improved considerably in the last few months, after having suffered in common with other textile firms in the U.S.A.

UNITED GLASS BOTTLE MANUFACTURERS

A final dividend of 5% on the ordinary shares is announced, bringing the total for the year to 7½%, which is the same as in the previous year.

MARKET REPORT

This Market Report is compiled from special information received from the manufacturers concerned.

Unless otherwise stated, the prices quoted below cover fair quantities net and naked at sellers' works.

The following alterations in prices are reported since the publication of the last Market Report (cf. CHEM. & IND., Mar. 3, 1933, p. 189).

TAR PRODUCTS

Acid Cresylic, 99/100.—11d.—1s. 8d. per gal. according to specification. Refined, 1s. 8d.—1s. 9d. per gal. Pale, 98%, 1s. 2d.—1s. 3d. per gal. 95%, 11d.—11½d. per gal. Dark, 10d. per gal.

GENERAL NOTES

Official Trade Intelligence

The Department of Overseas Trade (Development and Intelligence), 35, Old Queen Street, London, S.W.1, has received the following inquiries for British goods. *British firms may obtain further information by applying* to the Department and stating the specific number. *British India:* Paper (Director-General, India Store Department, Belvedere Road, Lambeth, S.E.1). *Canada:* Special equipment and materials for the pulp and paper industry (316). *Colombia:* Reclaimed lubricating oils (336). *Denmark:* Vegetable oils, chemicals (heavy and fine) (328). *France:* Nickel and alloys in ingots and manufactured into tubes (330). *South Africa:* Mild steel plates (G.X. 12,340).

Dyestuffs (Import Regulation) Act, 1920

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during February, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee:—The total number of applications received during the month was 532, of which 432 were from merchants or importers. To these should be added 6 cases outstanding on January 31, making a total for the month of 538. These were dealt with as follows: Granted, 525 (of which 519 were dealt with within 7 days of receipt); referred to British makers of similar products, 10 (all dealt with within 7 days of receipt); outstanding on February 28, 3. Of the total of 538 applications received, 529, or 98%, were dealt with within 7 days of receipt.

Import Duties Advisory Committee

The Import Duties Advisory Committee announces that it has decided not to make any recommendations in respect of the applications previously advertised for the addition to the Free List of "Lux" gas-purifying material (bog ore substitute) and for drawback in the case of cupro-nickel tubes for oil and water coolers.

The Committee also gives notice of applications for a reduction in the import duty on graphite electrodes of the following dimensions: slabs, 1000 mm. long by 175 mm. wide by 50 mm. thick, and rods, 300 to 350 mm. long by 50 mm. diameter: for drawback under Section 9 of the Finance Act, 1932, in the case of paraffin scale mixture in respect of the white paraffin scale used in its manufacture; and for drawback under Schedule II of the Import Duties Act in the case of machinery (including machine tools) and hand- or power-driven tools for engineering and woodworking and parts thereof.

Representations which interested parties may desire to make should be addressed to the Secretary of the Committee, Caxton House, Tothill Street, London, S.W.1, not later than March 20.

A Self-Priming Centrifugal Pump

Messrs. Drysdale & Co., Ltd., of Yoker, Glasgow, the well-known makers of centrifugal pumps, have recently put on the market a novel design of centrifugal pump of the self-priming type, which would appear to offer considerable advantages over the ordinary reciprocating pump so much in use at the present time. In this pump, which is known as the "Wee-Mac," the impeller is a plain disc with a number of blades arranged round the periphery, rotating inside a concentric casing having a wedged-shaped passage on each side of the impeller. The wedge-shaped passage on one side gradually decreases in area from the suction opening, while on the other side an opposite handed passage gradually widens until the discharge opening is reached. The water circulates in each of the blades itself where it is given an impulse. The discharge into the pipe passages is taken up by the next cell and so on until the discharge orifice is reached. A compound pumping effect is therefore obtained, which enables the pump to deliver at approximately three times the pressure of an ordinary centrifugal pump of the same proportions. The "Wee-Mac" pump has an extremely valuable feature in that it is self-priming, whilst it can deal with air-locks due to loops or rising in the suction pipes without the slightest difficulty. Tests have proved the pump capable of working with a suction lift of 28 ft. Various sizes, from 120 gallons per hour to 3000 gallons per hour, and for pressures up to 150 lb. per sq. in. can be supplied.

Japanese Production of Natural Gas

Figures given in the Journal of the Fuel Society of Japan indicate that the production of natural gas in Japan was greatly increased during the year 1931. During the year 1927 the production, expressed in units of 10,000 cb. ft., was 116,726, and no significant change had taken place by the end of 1929. During the next year however production amounted to 176,008 units, and in 1931 to 354,853, whilst a further increase is expected to be shown by the figure for 1932 when it becomes available.

Nickel and Monel Metal for Chemical Plant

Both nickel and its alloy monel metal are coming more and more into use for chemical plant, for which their properties of combined strength and corrosion-resistance make them especially suitable. A little booklet which summarizes in a concise manner the properties of the two metals, and their usefulness for various purposes in chemical works, has been issued by Henry Wiggin & Co., Ltd. Several useful tables are included, dealing with physical constants, technological properties, and mechanical properties, and a number of pieces of plant in nickel and monel metal are shown in photographs.